

51st
OHIO STATE UNIVERSITY
INTERNATIONAL SYMPOSIUM ON
MOLECULAR SPECTROSCOPY

JUNE 10-14, 1996

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College of Mathematical and Physical Sciences
Department of Chemistry
Department of Physics

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13. ABSTRACT (Maximum 200 words) This year there will be several mini-symposia. Kevin Lehmann , Princeton, and Frederic Stoeckel , Université J. Fourier, Grenoble, are organizing a session entitled "New Approaches to Absorption Spectroscopy." This topic includes intracavity laser absorption, cavity ring-down, laser frequency modulation, and related techniques. Invited speakers for this mini-symposium include John Hall , JILA; Frederic Stoeckel , Université J. Fourier; and Anthony O'Keefe , Los Gatos Research. Another mini-symposium is being organized by Ken Evenson , NIST, and Arlan Mantz , Connecticut College. The subject of this symposium is "Coherent IR Techniques/Spectroscopy" and will include talks concerning technical issues, design considerations, and spectral performance of relevance to our community as well as applications of these technologies. Invited speakers for the session include: Robert Curl , Rice; Ken Evenson , NIST; and Leo Hollberg , NIST. As usual we will have a special session on <i>ab initio</i> theory. The invited speaker will be Keiji Morokuma , Emory U.				
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Welcome to the 51st Ohio State University International Symposium on Molecular Spectroscopy

On behalf of the Executive Committee, Frank DeLucia, Eric Herbst, Weldon Mathews, Russell Pitzer, and myself, I wish to extend to all our Symposium guests a heartfelt welcome to Columbus and the second half century of the Ohio State University International Symposium on Molecular Spectroscopy. This year has been marked by the introduction of numerous electronic features to the Symposium. However, it is our desire that the meeting itself continues to be as personal and enjoyable as in the past as well as of great scientific significance. If we can help in any way, please do not hesitate to ask.

*Terry A. Miller
Symposium Chair*

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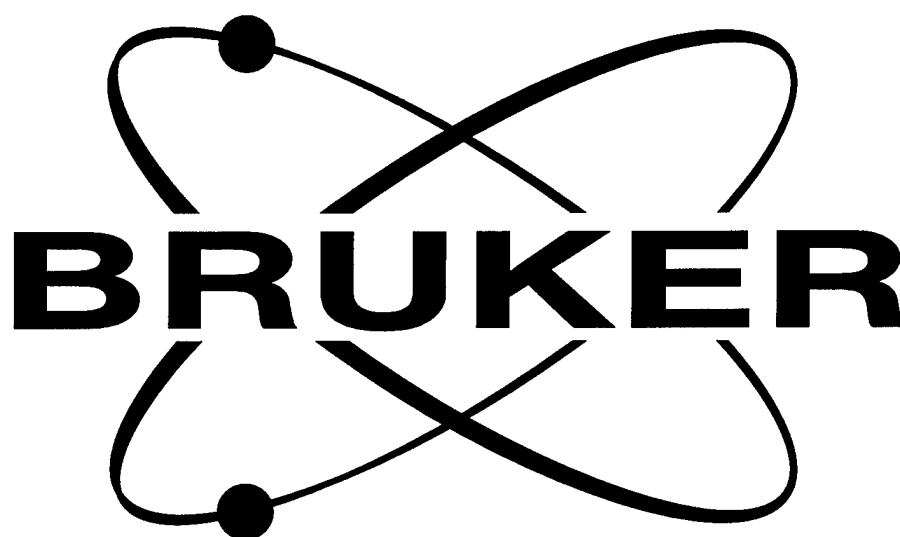
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51st OHIO STATE UNIVERSITY INTERNATIONAL SYMPOSIUM ON MOLECULAR SPECTROSCOPY JUNE 10-14, 1996

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* steering committee member

Special Sessions

This year there will be several mini-symposia. **Kevin Lehmann**, Princeton, and **Frederic Stoeckel**, Université J. Fourier, Grenoble, are organizing a session entitled "New Approaches to Absorption Spectroscopy." This topic includes intracavity laser absorption, cavity ring-down, laser frequency modulation, and related techniques. Invited speakers for this mini-symposium include **John Hall**, JILA; **Frederic Stoeckel**, Université J. Fourier; and **Anthony O'Keefe**, Los Gatos Research. Another mini-symposium is being organized by **Ken Evenson**, NIST, and **Arlan Mantz**, Connecticut College. The subject of this symposium is "Coherent IR Techniques/Spectroscopy" and will include talks concerning technical issues, design considerations, and spectral performance of relevance to our community as well as applications of these technologies. Invited speakers for the session include: **Robert Curl**, Rice; **Ken Evenson**, NIST; and **Leo Hollberg**, NIST. As usual we will have a special session on *ab initio* theory. The invited speaker will be **Keiji Morokuma**, Emory U.

Picnic

The picnic was deemed a big success last year and again will be held on Wednesday evening of the symposium. The cost of the picnic is included in your registration (at below cost to students), so that all may attend the event.

Sponsorship

We are pleased to announce that the **Army Office of Research** is continuing its long sponsorship of the Symposium. We are also receiving support from **The Ohio State University** through the **Chemistry and Physics Departments**, the **College of Mathematical and Physical Sciences**, and the **Office of Research**. In addition, this year we have added the concept of Corporate Sponsorship. Our Corporate sponsors are **Bruker Optics**, **Coherent Inc.**, and **Spectra-Physics**. As in the past, Coherent will sponsor the coffee and doughnuts, Bruker will defray part of the cost of printing the abstract book, and the support of Spectra-Physics will allow us to reduce the cost of the picnic for students. Our corporate sponsors will all have exhibits at the Symposium and we encourage you to visit their displays as well as those of our other exhibitors. In addition to our Corporate sponsors, **Instruments SA** and **General Valve** (a division of Parker Hannifin Corporation) have already announced their intentions to have exhibits at the Symposium and we expect several additional companies to join their ranks.

Rao Prize

The three Rao Prizes for the most outstanding student talks at the 1995 meeting will be presented. The winners are **Weng-Ching Hung**, National Tsing Hua University; **James Phillips**, University of Minnesota; **Pey-Shiun Yeh**, National Tsing Hua University. The Rao Prize was created by a group of spectroscopists who, as graduate students, benefited from the emphasis on graduate student participation, which has been a unique characteristic of the Symposium. This Symposium three more Rao Prizes will be awarded. The award is administered by a Prize Committee chaired by Arlan Mantz, Connecticut College, and comprised of Kevin Lehmann, Princeton University; John Muentner, University of Rochester; Michael Heaven, Emory University; Deanne Snively, Bowling Green State University; and Dan Willey, Allegheny College. Any questions or suggestions about the Prize should be addressed to the Committee.

MA. PLENARY SESSION

MONDAY, JUNE 10, 1996 – 8:45 AM

Room: AUDITORIUM INDEPENDENCE HALL

Chair: FRANK DE LUCIA, The Ohio State University, Columbus, Ohio

Welcome

15 min 8:45

Edward Hayes, Vice President for Research
The Ohio State University

MA01

LIPPINCOTT AWARD LECTURE

40 min 9:00

SPECTROSCOPY AND DYNAMICS OF HIGH SPIN ALKALI OLIGOMERS

G. SCOLES, *Department of Chemistry, Princeton University, Princeton, NJ 08544.*

MA02

40 min 9:45

SPECTROSCOPY OF DIATOMIC TRANSITION METAL MOLECULES

M. D. MORSE, *Department of Chemistry, University of Utah, Salt Lake City, UT 84112.*

Intermission

RAO AWARDS

20 min 10:50

Presentation of Awards by Arlan Mantz, Connecticut College

1995 Rao Award Winners

Weng-Ching Hung, National Tsing Hua University
James Phillips, University of Minnesota
Pey-Shiun Yeh, National Tsing Hua University

MA03

COBLENTZ PRIZE AND AWARD LECTURE

40 min 11:10

Presentation of Award by John Bertie, University of Alberta

SINGLE MOLECULE SPECTROSCOPY AND CHEMICAL DYNAMICS AT ROOM TEMPERATURE

X. SUNNEY XIE, *Pacific Northwest National Laboratory, Environmental Molecular Sciences Laboratory, Richland, WA 99352.*

ME. SYMPOSIUM: ABSORPTION SPECTROSCOPY

MONDAY, JUNE 14, 1996 – 1:30 PM

Room: 1153 SMITH LAB

Chair: FREDERIC STOECKEL, Université J. Fourier, Grenoble, France

ME01 30 min 1:30 INVITED TALK

CAVITY RINGDOWN SPECTROSCOPY: A LOOK INSIDE THE CAVITY

ANTHONY O'KEEFE, *Los Gatos Research, 1685 Plymouth Street, Mountain View CA 94043.*

ME02 15 min 2:05

THE SUPERPOSITION PRINCIPLE OF OPTICS AND CAVITY RING DOWN SPECTROSCOPY

K. K. LEHMANN, *Department of Chemistry, Princeton University, Princeton N. J. 08544*; D. ROMANINI, *Laboratoire de Spectrométrie Physique – CNRS URA 08, Université J. Fourier/Grenoble, B.P. 87 – 38402 Saint Martin d'Hères Cedex, France.*

ME03 15 min 2:22

A FOURIER TRANSFORM CAVITY RING DOWN SPECTROMETER

RICHARD ENGELN AND GERARD MEIJER, *Dept. of Molecular and Laser Physics, University of Nijmegen, Toernooiveld, 6526 ED Nijmegen, The Netherlands.*

ME04 15 min 2:39

DIRECT-ABSORPTION OBSERVATION OF A DOUBLY-FORBIDDEN ELECTRONIC TRANSITION IN DIACETYLENE USING CAVITY RING-DOWN SPECTROSCOPY

B. GILES, C. A. ARRINGTON, F. C. HAGEMEISTER, and T. S. ZWIER, *Department of Chemistry, Purdue University, West Lafayette, IN 47907-1393.*

ME05 15 min 2:56

INFRARED CAVITY RINGDOWN LASER ABSORPTION SPECTROSCOPY (IR-CRLAS) OF JET-COOLED WATER CLUSTERS

J. B. PAUL, C. P. COLLIER, R. J. SAYKALLY, *Department of Chemistry, University of California, Berkeley, CA 94720*; J. J. SCHERER, *Sandia National Laboratories, Livermore CA 94551.*

ME06 15 min 3:13

INFRARED CAVITY RINGDOWN LASER ABSORPTION SPECTROSCOPY (IR-CRLAS) IN LOW PRESSURE FLAMES

J. J. SCHERER and D. J. RAKESTRAW, *Combustion Research Facility, Sandia National Laboratories (M/S 9055), Livermore, CA 94551.*

ME07 15 min 3:30

QUANTITATIVE ABSORPTION MEASUREMENTS USING CAVITY RING DOWN SPECTROSCOPY

R. D. van ZEE, J. P. LOONEY, J. T. HODGES, *Process Measurements Division, National Institute of Standards and Technology, Gaithersburg, MD 20899.*

Intermission

ME08

10 min 4:00

LASER ABSORPTION SPECTROSCOPY OF TiCl^+ : ANALYSIS OF THE $[17.9]^3\Delta-X^3\Phi(0,0)$ BAND

L. A. KALEDIN, J. P. PARRISH, and M. C. HEAVEN, *Department of Chemistry, Emory University, Atlanta, GA 30322.*

ME09

15 min 4:12

DOUBLE MODULATION TECHNIQUE IN PULSED JET EXPERIMENTS: MOLECULAR VAN DER WAALS COMPLEXES

I. PAK, M. HEPP, D. ROTH, and G. WINNEWISSER, *I. Physikalisches Institut, Universität zu Köln, 50937 Köln, Germany.*

ME10

15 min 4:29

RESONANT FOUR-WAVE MIXING PROBES OF JET-COOLED POLYATOMIC MOLECULES: INFRARED DEGENERATE FOUR WAVE MIXING AND INFRARED/VISIBLE LASER INDUCED GRATING SPECTROSCOPIES

S. A. REID and Y. TANG, *Department of Chemistry, Marquette University, Milwaukee, WI 53201-1881.*

ME11

10 min 4:46

HIGH SENSITIVITY DETECTION OF TRICHLOROETHYLENE USING FREQUENCY-MODULATED TUNABLE DIODE LASERS

CHI KONG NG, KHOSROW NAMJOU, and EDWARD A. WHITTAKER, *Department of Physics and Engineering Physics, Stevens Institute of Technology, Hoboken, NJ 07030.*

ME12

15 min 4:58

INTRACAVITY SATURATED ABSORPTION SPECTROSCOPY OF THE 1.6-MICRON MOLECULAR OVERTONE BAND

H. SASADA and K. SUZUMURA, *Department of Physics, Faculty of Science and Technology, Keio University, Yokohama 223, Japan.*

ME13

10 min 5:15

PRESSURE BROADENING OF THE O_2 B BAND MEASURED BY CAVITY RING-DOWN SPECTROSCOPY

D. C. ROBIE, N. SEISER, *Department of Chemistry, Barnard College, New York, NY 10027.*

ME14

10 min 5:27

APPLICATION OF THE CAVITY RING-DOWN TECHNIQUE TO WATER VAPOUR CONTINUUM MEASUREMENTS

JOHN G. CORMIER AND JAMES R. DRUMMOND, *Department of Physics, University of Toronto, 60 St. George Street, Toronto, Ont., Canada, M5S 1A7.*

MF. MICROWAVE

MONDAY, JUNE 10, 1996 – 1:30 PM

Room: 1009 SMITH LAB

Chair: ANGELA HIGHT WALKER, NIST, Gaithersburg, Maryland

MF01 15 min 1:30

HYPERFINE STRUCTURE IN THE MICROWAVE SPECTRUM OF NF_3

STEWART E. NOVICK, WEI CHEN, MICHAEELEN R. MUNROW, *Department of Chemistry, Wesleyan University, Middletown, CT 06459*; KIMBERLEY J. GRANT, *Department of Chemistry, College of Saint Elizabeth, Morristown, NJ 07960*.

MF02 15 min 1:47

ROTATIONAL SPECTRA OF THE EXCITED VIBRATIONAL STATES OF NITRIC ACID

T. M. GOYETTE, *Department of Physics, The Ohio State University, 174 West 18th Avenue, Columbus, OH 43210-1106*; L. H. COUDERT, *Laboratoire de Physique moléculaire et Applications, CNRS, Université Pierre et Marie Curie, Cas Courrier 76, Tour 13, 4 Place Jussieu, F-75252 Paris Cedex 05, France*; L. C. OESTERLING, D. T. PETKIE, *Department of Physics, The Ohio State University, 174 West 18th Avenue, Columbus, OH 43210-1106*; R. A. BOOKER, *Department of Physics, University of North Carolina Asheville, 1 University Heights, Asheville, North Carolina 28804*; P. HELMINGER, *Department of Physics University of South Alabama, Mobile, AL 36688*; F. C. DE LUCIA, *Department of Physics, The Ohio State University, 174 West 18th Avenue, Columbus, OH 43210-1106*.

MF03 15 min 2:04

MICROWAVE SPECTRA OF NaBH_4 AND KBH_4 IN EXCITED VIBRATIONAL STATES

Y. KAWASHIMA, *Department of Chemical Technology, Kanagawa Institute of Technology, Atsugi, Kanagawa 243-02, Japan*; E. HIROTA, *The Graduate University for Advanced Studies, Hayama, Kanagawa, 240-01, Japan*; O. N. ULENIKOV and A. B. MALIKOVA, *Physics Department, Tomsk State University 634050, Tomsk, Russia*.

MF04 15 min 2:21

ROTATIONAL SPECTRUM, STRUCTURE AND DIPOLE MOMENT OF DESFLURANE

R. D. SUENRAM, A. R. HIGHT WALKER, and F. J. LOVAS, *Optical Technology Division, NIST, Gaithersburg, MD 20899*.

MF05 15 min 2:38

MW AND FTFIR TRANSITIONS OF $^{13}\text{CH}_3\text{OH}$ REVISITED AND REVIEW OF MW SPECTRA OF CH_3OH AND $^{13}\text{CH}_3\text{OH}$ OF ASTROPHYSICAL INTEREST

LI-HONG XU, *Department of Physical Sciences, University of New Brunswick, Saint John, N.B., Canada E2L 4L5*; M. S. WALSH, R. M. LEES, *Department of Physics, University of New Brunswick, Fredericton, N.B., Canada E3B 5A3*; F. J. LOVAS, *Radiometric Physics Division, National Institute of Standards and Technology, Gaithersburg, MD 20899*.

MF06

15 min 2:55

METHANOL AS A FLEXIBLE MODEL

MIRZA A. MEKHTIEV^a, PETER D. GODFREY, *Chemistry Department, Monash University, Clayton, Victoria 3168, Australia*; VIKTOR SZALAY, *Research Laboratory for Crystal Physics, Hungarian Academy of Sciences, 1502 Budapest, Pf. 132, Hungary*.

^aPresent address: Molecular Physics Division, National Institute of Standards and Technology, Gaithersburg, MD 20899

MF07

15 min 3:12

APPLICATIONS OF EFFECTIVE ROTATIONAL HAMILTONIANS FOR TWO-ROTOR MOLECULES

PETER GRONER, *Department of Chemistry, University of Missouri - Kansas City, Kansas City, MO 64110*.

Intermission

MF08

15 min 3:45

THE SUBMILLIMETER SPECTRUM OF THE GROUND HYDROXYL TORSIONAL STATE OF ETHYL ALCOHOL (CH₃CH₂OH)

J. C. PEARSON, *Jet Propulsion Laboratory, California Institute of Technology, Mail Stop 183-301, 4800 Oak Grove Dr., Pasadena, CA 91109*; K. V. L. N. SASTRY, *Department of Physics, University of New Brunswick, Fredericton, New Brunswick, E3B 5A3 Canada*; E. HERBST and F. C. DE LUCIA, *Department of Physics, The Ohio State University, 174 W. 18th Ave., Columbus, OH 43210*.

MF09

15 min 4:02

THE GROUND STATE TORSION-ROTATION SPECTRUM OF PROPARGYL ALCOHOL (HCCCH₂OH)

J. C. PEARSON, *Jet Propulsion Laboratory, California Institute of Technology, Mail Stop 183-301, 4800 Oak Grove Dr., Pasadena, CA 91109*.

MF10

10 min 4:19

MICROWAVE-MICROWAVE DOUBLE-RESONANCE ASSIGNMENT OF THE GAUCHE CONFORMER OF METHYL VINYL ETHER

DAVID A. MCWHORTER, SAM CUPP, CHUNG YI LEE and BROOKS H. PATE, *Department of Chemistry, University of Virginia, Charlottesville, VA 22901*.

MF11

15 min 4:31

MICROWAVE SPECTRA OF MOLECULES WITH MULTIPLE CONFORMATIONS: 2,2,4-TRIMETHYLPENTANE

A. R. HIGHT WALKER, R. D. SUENRAM, G. T. FRASER, *Optical Technology Division, National Institute of Standards and Technology, Gaithersburg, MD 20899*; K. K. IRIKURA, *Chemical Kinetics and Thermodynamics Division, National Institute of Standards and Technology, Gaithersburg, MD 20899*.

MF12

15 min 4:48

CHARACTERIZATION OF (Z)- AND (E)-ETHANETHIAL S-OXIDE BY PULSED-BEAM FT-MW SPECTROSCOPY

C. W. GILLIES, *Department of Chemistry, Rensselaer Polytechnic Institute, Troy, NY 12180*; J. Z. GILLIES, *Department of Chemistry, Siena College, Loudonville, NY 12211*; J. -U. GRABOW, *Molecular Physics Division, National Institute of Standards and Technology, Gaithersburg, MD 20899*.

MF13

15 min 5:05

IN SITU DETECTION AND MECHANISM OF FORMATION OF THE ONION LACHRYMATOR, (Z)-PROPANETHIAL S-OXIDE, BY PULSED-BEAM FT-MW SPECTROSCOPY

C. W. GILLIES, *Department of Chemistry, Rensselaer Polytechnic Institute, Troy, NY 12180*; J. Z. GILLIES, *Department of Chemistry, Siena College, Loudonville, NY 12211*; J. -U. GRABOW, *Molecular Physics Division, National Institute of Standards and Technology, Gaithersburg, MD 20899*.

MF14

15 min 5:22

THE CONFORMATION AND INTERNAL ROTATION BARRIER IN BENZYL FLUORIDE

ROBERT K. BOHN, *Department of Chemistry, U. of Connecticut, Storrs, CT 06269-4060*; STERLING A. SORENSON, NANCY S. TRUE, *Department of Chemistry, U. of California, Davis, CA 95616*; THOMAS BRUPBACHER, MICHAEL C. L. GERRY, *Department of Chemistry, U. of British Columbia, Vancouver, BC V6T 1Z1*; WOLFGANG JAEGER, *Department of Chemistry, U. of Alberta, Edmonton, Alberta T6G 2G2*.

MG. RADICALS AND IONS
MONDAY, JUNE 14, 1996 – 1:30 PM
Room: 1005 SMITH LAB

Chair: DAVID POWERS, The Ohio State University, Columbus, Ohio

MG01 **10 min 1:30**

THE INFRARED SPECTRUM OF HBO

P. COLARUSSO, K.-Q. ZHANG, and P.F. BERNATH, *Centre for Molecular Beams and Laser Chemistry, University of Waterloo, Waterloo, Ontario, Canada, N2L 3G1.*

MG02 **10 min 1:42**

INFRARED SPECTROSCOPY OF BrCNO

KEQING ZHANG, B. GUO, P. BERNATH, *Centre for Molecular Beams and Laser Chemistry, Department of Chemistry, University of Waterloo, Waterloo, Ontario, Canada, N2L 3G1*; T. PASINSZKI, N. P. C. WESTWOOD, *Department of Chemistry and Biochemistry, University of Guelph, Guelph, Ontario, Canada, N1G 2W1.*

MG03 **15 min 1:54**

INFRARED EMISSION SPECTRA OF MOLECULAR IONS IN FAST ION BEAMS

M. D. TISSANDIER, A. D. EARHART, and J. V. COE, *Department of Chemistry, The Ohio State University, Columbus, OH 43210-1173.*

MG04 **15 min 2:11**

EXCITATION TEMPERATURES DETERMINED FROM H_3^+ HOT BAND EMISSION IN THE JOVIAN IONOSPHERE

M. -F. JAGOD, T. OKA, *Department of Chemistry and Department of Astronomy and Astrophysics, and the Enrico Fermi Institute, The University of Chicago, Chicago, IL 60637*; T. R. GEBALLE, *Joint Astronomy Centre, 660 N. A'ohōkū Place, University Park, Hilo HI 96720.*

MG05 **15 min 2:28**

OBSERVATION OF A NONTHERMAL ORTHO-TO-PARA RATIO OF H_3^+ IN HYDROGEN PLASMAS: SPIN SELECTION RULES IN PLASMA CHEMISTRY

D. UY, *Department of Chemistry and Department of Astronomy and Astrophysics, The University of Chicago, Chicago, IL 60637*; M. CORDONNIER, *Laboratoire de Spectroscopie Hertzienne, Université des Sciences et Technologies de Lille, 59655 Villeneuve d'Ascq, France*; R. M. DICKSON, K. E. KERR and T. OKA, *Department of Chemistry and Department of Astronomy and Astrophysics, The University of Chicago, Chicago, IL 60637.*

MG06 **15 min 2:45**

OBSERVATION OF $\Delta |k-l|=3$ TRANSITIONS IN THE ν_3 BAND OF THE H_3O^+

D. UY, E. WHITE, and T. OKA, *Department of Chemistry and Department of Astronomy and Astrophysics, The University of Chicago, Chicago, IL 60637.*

MG07

15 min 3:02

TIME-RESOLVED DIODE LASER SPECTROSCOPY OF THE ν_3 BAND OF THE IRON DICARBONYL RADICAL $\text{Fe}(\text{CO})_2$

KEIICHI TANAKA, KEISUKE UEMURA, and TAKEHIKO TANAKA, *Department of Chemistry, Faculty of Science, Kyushu University 33, Hakozaki, Higashiku Fukuoka 812-81, Japan.*

Intermission

MG08

15 min 3:30

MID-INFRARED SPECTROSCOPY OF IONIC PROTON-BOUND COMPLEXES: INTERMOLECULAR INTERACTION AND SOLVATION EFFECTS

OTTO DOPFER, SERGEY A. NIZKORODOV, MARKUS MEUWLY, JOHN P. MAIER, *Institut für Physikalische Chemie, Universität Basel, Klingelbergstrasse 80, CH-4056 Basel, Switzerland*; EVAN J. BIESKE, *School of Chemistry, University of Melbourne, Parkville, Victoria 3052, Australia.*

MG09

15 min 3:47

SPIN-ROTATION AND HYPERFINE SPECTROSCOPY IN THE NEAR-IR: A STUDY OF THE METHYL RADICAL

SCOTT DAVIS, DAVID T. ANDERSON, and DAVID J. NESBITT, *JILA, National Institute of Standards and Technology and Department of Chemistry and Biochemistry, University of Colorado, Boulder, CO 80309-0440.*

MG10

15 min 4:04

HIGH RESOLUTION INFRARED ABSORPTION SPECTROSCOPY OF JET-COOLED MOLECULAR IONS

SCOTT DAVIS, DAVID T. ANDERSON, and DAVID J. NESBITT, *JILA, National Institute of Standards and Technology and Department of Chemistry and Biochemistry, University of Colorado, Boulder, CO 80309-0440.*

MG11

15 min 4:21

OBSERVATION OF ν_4 BAND TRANSITIONS OF NH_4^+ AND ND_4^+

CHANGHONG XIA, MARIA M. SANZ and STEPHEN C. FOSTER, *Department of Chemistry, Mississippi State University Mississippi State, MS 39762-9573.*

MG12

15 min 4:38

THE GROUND-STATE OF PROTONATED CARBONYL SULFIDE, HOCS^+ OR OCSH^+ ?

MARIA M. SANZ, CHANGHONG XIA, STEPHEN C. FOSTER and SVEIN SAEBO, *Department of Chemistry, Mississippi State University Mississippi State, MS 39762-9573.*

MG13

15 min 4:55

DIODE LASER TRANSIENT ABSORPTION SPECTRUM OF THE ETHYL RADICAL

TREVOR J. SEARS, PEI JIN, *Department of Chemistry, Brookhaven National Laboratory, Upton, NY 11973-5000*; PHILIP M. JOHNSON, *Department of Chemistry, State University of New York, Stony Brook, NY 11974*; SUSAN OATIS, *Department of Chemistry, Long Island University, Southampton, NY 11968.*

MG14**5 min 5:12****INFRARED DIODE LASER SPECTROSCOPY OF THE X²II CCl RADICAL**

PEI JIN, BOR-CHEN CHANG, and TREVOR J. SEARS, *Department of Chemistry, Brookhaven National Laboratory, Upton, NY 11973-5000.*

MG15**15 min 5:19****CONCENTRATION MODULATION TECHNIQUE FOR A CONTINUOUS-SCAN FTIR SPECTROMETER**

TAKASHI IMAJO, SHINOBU INUI, KEIICHI TANAKA, and TAKEHIKO TANAKA, *Department of Chemistry, Faculty of Science, Kyushu University 33, Hakozaki, Higashi ku, Fukuoka 812-81, Japan.*

MG16**10 min 5:36****HIGH RESOLUTION FTIR SPECTROSCOPY OF THE PO RADICAL**

DONGBING WANG, TAKASHI IMAJO, KEIICHI TANAKA, and TAKEHIKO TANAKA, *Department of Chemistry, Faculty of Science, Kyushu University 33, Hakozaki, Higashiku, Fukuoka 812-81, Japan.*

MH. INFRARED

MONDAY, JUNE 10, 1996 – 1:30 PM

Room: 1008 EVANS LAB

Chair: JEAN-MARIE FLAUD, Universite Pierre et Marie Curie, Paris, France

MH01 **15 min 1:30**

LINE MIXING SUM RULES FOR QUASIELASTIC COLLISIONS IN MULTIPLY SPECTRA

A. S. PINE, *Optical Technology Division, National Institute of Standards and Technology, Gaithersburg, MD 20899.*

MH02 **15 min 1:47**

N₂ AND Ar BROADENING AND LINE MIXING IN THE P AND R BRANCHES OF THE ν_3 BAND OF METHANE

A. S. PINE, *Optical Technology Division, National Institute of Standards and Technology, Gaithersburg, MD 20899.*

MH03 **15 min 2:04**

M-RESOLVED COLLISION-INDUCED ROTATIONAL ENERGY/ALIGNMENT TRANSFER IN CH₄

STEPHEN L. COY, *MIT Chemistry, 77 Mass. Ave., Cambridge, MA 02139*; JODY J. KLAASSEN, *JILA, Boulder, CO*; and JEFFREY I. STEINFELD, *MIT Chemistry, 77 Mass. Ave., Cambridge, MA 02139.*

MH04 **15 min 2:21**

PRESSURE SHIFTS IN THE ν_3 -BAND OF NO₂ INDUCED BY COLLISIONS WITH NOBLE GASES, N₂, H₂, D₂, O₂, CO₂, AND SO₂

A. KISSEL, *Optisches Institut der Technischen Universität Berlin, Sekr. PN 0-1, Hardenbergstr. 36, 10623 Berlin, Germany*; S. BOUAZZA, *permanent address: Département de Physique, Université de Champagne-Ardenne Reims, France*; B. SUMPF^a, H.-D. KRONFELDT, *Optisches Institut der Technischen Universität Berlin, Sekr. PN 0-1, Hardenbergstr. 36, 10623 Berlin, Germany.*

^aB.S. acknowledges a grant from the *Deutsche Forschungsgemeinschaft*

MH05 **15 min 2:38**

SELF- AND FOREIGN GAS BROADENING IN THE $\nu_1 + \nu_3$ BAND OF SO₂^a

B. SUMPF^b, D. REHLE, H.-D. KRONFELDT, *Optisches Institut der Technischen Universität Berlin, Sekr. PN 0-1, Hardenbergstr. 36, 10623 Berlin, Germany*; V.V. LAZAREV^c, *Institute of Atmospheric Optics, Siberian Branch, Russian Academy of Sciences, 1 Akademicheskii av., Tomsk 634055 Russia.*

^aThis project was supported by the *Deutsche Forschungsgemeinschaft*

^bB.S. acknowledges a grant from the *Deutsche Forschungsgemeinschaft*

^cV.V.L. acknowledges a grant from the *Deutscher Akademischer Austauschdienst*

MH06 **15 min 2:55**

TEMPERATURE AND QUANTUM NUMBER DEPENDENCE OF BROADENING COEFFICIENTS IN THE ν_3 BAND OF SO₂

B. SUMPF^a, M. SCHÖNE, H.-D. KRONFELDT, *Optisches Institut der Technischen Universität Berlin, Sekr. PN 0-1, Hardenbergstr. 36, 10623 Berlin, Germany.*

^aB.S. acknowledges a grant from the *Deutsche Forschungsgemeinschaft*

MH07

15 min 3:12

INFRARED ABSORPTION CROSS-SECTIONS AND BAND STRENGTHS OF HFC-32 VAPOUR (DIFLUOROMETHANE)

G. DUXBURY^a, K. SMITH, *Department of Physics and Applied Physics, Strathclyde University, Glasgow G4 0NG, Scotland, UK*; D. NEWNHAN, M. PAGE, and JOHN BALLARD, *Atmospheric Science Division, Space Science Department, Rutherford Appleton Laboratory, Chilton, Didcot, OX11 0QX, UK.*

^avisiting fellow at JILA

Intermission

MH08

15 min 3:45

HITEMP-HIGH-TEMPERATURE MOLECULAR ABSORPTION DATABASE FOR H₂O, CO₂ AND CO

LAURENCE S. ROTHMAN, ROBERT L. HAWKINS, *Geophysics Directorate, Hanscom AFB, MA 01731-3010*; RICHARD B. WATTSON, *Stewart Radiance Laboratory, Utah State University, Bedford, MA 01730*; ROBERT R. GAMACHE, *Center for Atmospheric Research, Univ. of Mass. Lowell, Lowell MA 01854*; and JOHN SCHROEDER, *Ontar Corp., 9 Village Way, N. Andover MA 01845-2000.*

MH09

15 min 4:02

VIBRATIONAL ENERGIES AND ROTATIONAL CONSTANTS OF ¹²C¹⁶O₂

D. CHRIS BENNER, V. MALATHY DEVI, *Department of Physics, College of William and Mary, Williamsburg, VA 23187-8795*; CURTIS P. RINSLAND and MARY ANN H. SMITH, *Atmospheric Sciences Division, NASA Langley Research Center, Mail Stop 401A, Hampton, VA 23681-0001.*

MH10

10 min 4:19

ABSOLUTE INTENSITIES OF CO₂ LINES IN THE 1830 TO 4000 cm⁻¹ SPECTRAL REGION

V. MALATHY DEVI, D. CHRIS BENNER, *Department of Physics, The College of William and Mary, Williamsburg, VA 23187-8795*; C. P. RINSLAND and M. A. H. SMITH, *Atmospheric Sciences Division, NASA Langley Research Center, Mail Stop 401A, Hampton, VA 23681-0001.*

MH11

15 min 4:31

COMPARISON OF CO₂ ABSOLUTE INTENSITIES FOR BANDS NEAR 4000 cm⁻¹

D. CHRIS BENNER, *Department of Physics, College of William and Mary, Williamsburg, VA 23187-8795*; LAWRENCE P. GIVER, CHARLES CHACKERIAN, Jr., *NASA Ames Research Center, Moffett Field, CA 94035-1000*; V. MALATHY DEVI, *Department of Physics, College of William and Mary, Williamsburg, VA 23187-8795*; LINDA R. BROWN, *Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA 91109*; CURTIS P. RINSLAND and MARY ANN H. SMITH, *Atmospheric Sciences Division, NASA Langley Research Center, Mail Stop 401A, Hampton, VA 23681-0001.*

MH12

15 min 4:48

THE HOT BANDS OF METHANE BETWEEN 5 AND 10 MICRONS

O. OUARDI, J. C. HILICO, M. LOETE, *Laboratoire de Physique de l'Université de Bourgogne*; and L. R. BROWN, *Jet Propulsion Laboratory, California Institute of Technology, 4800 Oak Grove Drive, Pasadena, California 91109.*

MH13**15 min 5:05****SELF-BROADENING COEFFICIENTS FROM FTIR MEASUREMENTS OF H₂O**

KAREN A. KEPPLER, K. NARAHARI RAO, *Department of Physics, The Ohio State University, Columbus, OH 43210-1106*; V.I. G. TYUTEREV, S. N. MIKHAILENKO, *GSMA U.A. CNRS D 1434, Faculté des Sciences, BP 347-51062 Reims Cédex France*; G. Ch. MELLAU, S. KLEE, B. P. WINNEWISSER, and M. WINNEWISSER, *Physikalisch-Chemisches Institut, Justus-Liebig-Universität Giessen, D-35392 Giessen, Germany*.

MH14**15 min 5:22****MEASUREMENTS OF O₃ LINE INTENSITIES IN THE ν_3 BAND**

M. A. H. SMITH, C. P. RINSLAND, *Atmospheric Sciences Division, NASA Langley Research Center, Mail Stop 401A, Hampton, VA 23681-0001*; V. MALATHY DEVI, and D. CHRIS BENNER, *Department of Physics, The College of William and Mary, Williamsburg, VA 23187-8795*.

MH15**10 min 5:39****INVESTIGATION OF THE WATER VAPOR LINESHIFTS IN THE (010)-(000) AND (011)-(000) BANDS**

A. VALENTIN, F. RACHET, *Université de Pierre et Marie Curie, 75005 Paris, France*; A. BYKOV, N. LAVRENT'EVA, V. SAVEL'EV, L. SINITSA, and A. SOLODOV, *Institute of Atmospheric Optics, Tomsk, 634055 Russia*.

MH16*Post-deadline Abstract***15 min 5:51****SYNCHRONOUSLY SCANNED OPO CARS: A NEW TOOL FOR MOLECULAR SPECTROSCOPY**

PETER C. CHEN, *Spelman College, 350 Spelman Ln. Box 307, Atlanta, Georgia, 30314*.

TA. SYMPOSIUM: ABSORPTION SPECTROSCOPY

TUESDAY, JUNE 11, 1996 – 8:30 AM

Room: 1153 SMITH LAB

Chair: ANTHONY O'KEEFE, Los Gatos Research, Mountain View, California.

TA01 **INVITED TALK** **30 min 8:30**
 NEW ASPECTS OF THE INTRACAVITY LASER ABSORPTION SPECTROSCOPY

F. STOECKEL, *Laboratoire de Spectrométrie Physique Université J. Fourier/CNRS/Grenoble BP87 38402 Saint Martin d'Hères Cedex France.*

TA02 **15 min 9:05**
 INTRACAVITY LASER ABSORPTION SPECTROSCOPY AS A LABORATORY TECHNIQUE: STATE OF THE ART

A. KACHANOV, *Laboratoire de Spectrométrie Physique Université J. Fourier/CNRS/Grenoble BP87 38402 Saint Martin d'Hères Cedex France.*

TA03 **15 min 9:22**
 SENSITIVITY LIMITS OF INTRACAVITY ABSORPTION SPECTROSCOPY

V.M. BAEV, J. SIERKS, T. LATZ, R. BOEHM, J. HUENKEMEIER, P.E. TOSCHEK, *Institut fuer Laser-Physik, Universitaet Hamburg, D-20355 Hamburg, Germany.*

TA04 **10 min 9:39**
 ABSORPTION COEFFICIENTS AND BAND STRENGTHS FOR THE 703 NM AND 727 NM BANDS OF METHANE AT 77 K

JAMES J. O'BRIEN and KULDIP SINGH, *Department of Chemistry and Center for Molecular Electronics, University of Missouri-St. Louis, St. Louis, MO 63121-4499.*

TA05 **10 min 9:51**
 INTRACAVITY LASER SPECTROSCOPY AT ULTRA-HIGH RESOLUTION - QUANTITATIVE DETERMINATION OF LINE STRENGTHS USING A NEW METHOD FOR DATA ACQUISITION

JAMES J. O'BRIEN, *Department of Chemistry and Center for Molecular Electronics, University of Missouri-St. Louis, St. Louis, MO 63121-4499.*

TA06 **15 min 10:03**
 INTRACAVITY LASER ABSORPTION SPECTROSCOPY OF FLAMES. HCO RADICAL DETECTION IN METHANE/AIR FLAME

SERGEY CHESKIS, *School of Chemistry, Sackler Faculty of Exact Sciences, Tel Aviv University, Ramat Aviv, Tel Aviv 69978, Israel;* VLADIMIR A. LOZOVSKY, *Institute of Chemical Physics, Russian Academy of Sciences, Kosygina str. 4, 117977 Moscow, Russia.*

TA07

10 min 10:20

TIME RESOLVED ICLAS SPECTROSCOPY OF HO₂ RADICAL

V. A. LOZOVSKY, V. P. BULATOV, F. N. DZEGILENKO, O. M. SARKISOV, *Department of Kinetics and Catalysis, N.N. Semenov Institute of Chemical Physics, Kosygina st. 4, 117977 Moscow, Russia*; YU. V. MATYAGIN, E. A. SVIRIDENKOV, *Lebedev Physical Institute, Leninsky prospekt 53, 117924 Moscow Russia*.

Intermission

TA08

10 min 10:45

INTRACAVITY LASER SPECTROSCOPY

N. A. RASPOPOV, E. A. SVIRIDENKOV, and S. E. VINOGRADOV ^a, *Lebedev Physical Institute, Leninsky pr. 53, Moscow, 117924 Russia*.

^aSupport by Soros International Science Foundation research grant and Russian Foundation for Basic Research grant is gratefully acknowledged

TA09

15 min 10:57

ULTRASENSITIVE DUAL-BEAM ABSORPTION SPECTROSCOPY, BASED ON WAVELENGTH-MODULATION TECHNIQUE AND LOGARITHMIC NOISE CANCELING

Yu. KURITSYN and V. LIGUER, *Institute of Spectroscopy, Russian Academy of Science, 142092 Troitsk Moscow Region, Russia*.

TA10

15 min 11:14

INTRACAVITY ABSORPTION VERSUS RING-DOWN, RELATIVE PERFORMANCE

D. ROMANINI, A. KACHANOV, *Laboratoire de Spectrométrie Physique Université J. Fourier/CNRS/Grenoble BP87 38402 Saint Martin d'Hères Cedex France*.

TA11

10 min 11:31

QUANTITATIVE ABSORPTION PARAMETERS FOR LINES IN THE 790 NM BAND OF WATER OBTAINED USING INTRACAVITY LASER SPECTROSCOPY WITH A Ti:SAPPHIRE LASER

BALAZS L. KALMAR and JAMES J. O'BRIEN, *Department of Chemistry and Center for Molecular Electronics, University of Missouri-St. Louis, St. Louis, MO 63121-4499*.

TA12

10 min 11:43

INTERCAVITY LASER ABSORPTION SPECTROMETER BASED ON YAG: CR⁴⁺ LASER FOR 1340 – 1680 nm SPECTRAL REGION

A. A. KACHANOV, *Institute for Spectroscopy, Russia Academy of Sciences, Troitsk 142092, Moscow Region, Russia*; S. A. KOVALENKO, *Institute of Chemical Physics, Russia Academy of Sciences, Kosygina Street, Moscow B-334, 117977, Russia*; A. G. OKHRIMCHUK, D. V. SMOLIN, AND A. V. SHESTAKOV, *POLUS Institute, 3 Vvedensky Street, Moscow 117342, Russia*.

TA13

10 min 11:55

MEASUREMENTS OF GROUND STATE OXYGEN, WATER VAPOR AND TEMPERATURE IN CHEMICAL OXYGEN-IODINE LASER BY Ti:SAPPHIRE LASER-BASED INTRACAVITY LASER SPECTROSCOPY

M. P. FROLOV, Yu. P. PODMARKOV ^b, *Lebedev Physical Institute, Leninsky pr. 53, Moscow, 117924 Russia*.

^bSupport by Russian Foundation for Basic Research grant is gratefully acknowledged

TB. ELECTRONIC (LARGE)
TUESDAY, JUNE 11, 1996 – 8:30 AM
Room: 1009 SMITH LAB

Chair: WAYNE SINCLAIR, University of Pittsburgh, Pittsburgh, Pennsylvania
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TB01 **15 min 8:30**

VIBRATIONAL ACTIVITY IN THE S_1 - S_0 SPECTROSCOPY OF PARA, META, AND ORTHOFLUOROTOLUENES

TODD STONE, QUAN JU, CHARLES S. PARMENTER, *Department of Chemistry, Indiana University, Bloomington, IN 47405*; AND ZHONG-QUAN ZHAO, *ThermoTrex Corp, 9550 Distribution Ave., San Diego, CA 92121-2306*.

TB02 **15 min 8:47**

INTERACTION BETWEEN VIBRATIONS AND INTERNAL ROTATION IN S_1 M-FLUOROTOLUENE AS SEEN IN THE S_1 - S_0 SPECTROSCOPY

QUAN JU, AND CHARLES S. PARMENTER, *Department of Chemistry, Indiana University, Bloomington, IN 47405*.

TB03 **15 min 9:04**

ELECTRONIC SPECTROSCOPY OF HYDROCINNAMIC ACID

J. A. DICKINSON, P. W. JOIREMAN, R. W. RANDALL, E. G. ROBERTSON, and J. P. SIMONS, *Physical and Theoretical Chemistry Laboratory, Oxford University, South Parks Road, Oxford*.

TB04 **15 min 9:21**

SPECTROSCOPY OF SOME N-PHENYL AMIDES. STRUCTURES AND RELATIVE STABILITIES OF THE CIS AND TRANS ISOMERS

VICTORIA P. MANEA, JOHN R. CABLE, *Department of Chemistry and Center for Photochemical Sciences, Bowling Green State University, Bowling Green, OH 43403*.

TB05 **15 min 9:38**

EVIDENCE FOR S_1/S_2 ELECTRONIC STATE MIXING IN THE $S_1 \leftarrow S_0$ FLUORESCENCE EXCITATION SPECTRUM OF 1-NAPHTHOL

SUSAN HUMPHREY and DAVID W. PRATT, *Department of Chemistry, University of Pittsburgh, Pittsburgh, PA 15260*.

TB06 **15 min 9:55**

$S_1 \leftarrow S_0$ TRANSITION MOMENT ORIENTATIONS IN AROMATIC ETHERS

JASON W. RIBBLETT and DAVID W. PRATT, *Department of Chemistry, University of Pittsburgh, Pittsburgh, PA 15260*.

Intermission

TB07

15 min 10:30

RYDBERG TRANSITIONS ORIGINATING AT METAL-LOCALIZED ORBITALS IN LARGE POLYATOMIC MOLECULES: A GAS-PHASE SPECTROSCOPIC STUDY OF TRANSITION-METAL SANDWICH COMPLEXES

S. Yu. KETKOV, *G.A. Razuvaev Institute of Organometallic Chemistry of Russian Academy of Sciences, Nizhny Novgorod 603600, Russia.*

TB08

15 min 10:47

HUND'S CASE (a) -CASE (b) TRANSITION IN THE SINGLET-TRIPLET SPECTRUM OF PRYAZINE IN A SUPER-SONIC JET

EMILE S. MEDVEDEV, *Institute of Chemical Physics, Russian Academy of Sciences, 142432 Chernogolovka, Moscow, Russia*; DAVID W. PRATT, *Department of Chemistry, University of Pittsburgh, Pittsburgh, PA 15260.*

TB09

10 min 11:04

ROTATIONALLY RESOLVED COHERENT ION DIP SPECTROSCOPY OF HIGH LYING GROUND STATE VAN DER WAALS VIBRATIONS OF THE BENZENE · Ar COMPLEX

R. NEUHAUSER, J. BRAUN, and H.J. NEUSSER, *Institut für Physikalische und Theoretische Chemie, Technische Universität München, Lichtenbergstr. 4, D-85748 Garching, Germany.*

TB10

15 min 11:16

ROTATIONALLY RESOLVED HIGH ($n > 100$) RYDBERG STATES IN A POLYATOMIC MOLECULE

R. NEUHAUSER, K. SIGLOW, and H.J. NEUSSER, *Institut für Physikalische und Theoretische Chemie, Technische Universität München, Lichtenbergstr. 4, D-85748 Garching, Germany.*

TB11

15 min 11:33

JET SPECTROSCOPY OF THE $D_1\ 2^2B_1 - D_0\ 1^2B_1$ ELECTRONIC TRANSITION OF THE *p*-CYANO BENZYL RADICAL

MASARU FUKUSHIMA, *Advanced Technology Research Center, Mitsubishi Heavy Industries, LTD., Sachiura, Kanazawa, Yokohama 236, Japan*; KINICHI OBI, *Department of Chemistry, Tokyo Institute of Technology, Ohokayama, Meguro, Tokyo 152, Japan.*

TB12

15 min 11:50

TOWARDS THE LIF SPECTRUM OF PHENYLNITRENE: YET ANOTHER PRECURSOR THAT YIELDS SOMETHING ELSE

MICHAEL B. PUSHKARSKY, DAVID E. POWERS, CHRISTOPHER C. CARTER, JAMES M. WILLIAMSON, TIMOTHY A. BARCKHOLTZ AND TERRY A. MILLER, *Laser Spectroscopy Facility, Department of Chemistry, The Ohio State University, Columbus, Ohio 43210.*

TC. THEORY

TUESDAY, JUNE 11, 1996 – 8:30 AM

Room: 1005 SMITH LAB

Chair: ANNE McCOY, The Ohio State University, Columbus, Ohio

TC01 15 min 8:30

ROTATIONALLY INDUCED STABLE QUANTUM MECHANICAL STATES

J. KONARSKI, Faculty of Chemistry, A.Mickiewicz University of Poznań, Grunwaldzka 6, 60-780 Poznań, Poland.

TC02 15 min 8:47

THE POTENTIAL ENERGY SURFACE OF H_2^{16}O

OLEG L. POLYANSKY, Department of Physics and Astronomy, University College London, Gower Street, London WC1E 6BT, UK; PER JENSEN, FB 9-Theoretische Chemie, Bergische Universität- Gesamthochschule Wuppertal, D-42097 Wuppertal, Germany; JONATHAN TENNYSON, Department of Physics and Astronomy, University College London, Gower Street, London WC1E 6BT, UK.

TC03 15 min 9:04

FITTING OF A PES FOR ROVIBRATIONAL CALCULATIONS ON NO_2

JEREMY H. SCHRYBER, OLEG POLYANSKY, JONATHAN TENNYSON, Department of Physics and Astronomy, University College London, Gower Street, London WC1E 6BT; PER JENSEN, Physikalisch-Chemisches Institut, Justus-Liebig-Universität Giessen, Heinrich-Buff-Ring 58, D-35392 Giessen, Germany.

TC04 15 min 9:21

VIBRATIONAL ENERGY REDISTRIBUTION (IVR): NEW MODELS AND COMPUTATIONAL APPROACHES

MARTIN GRUEBELE, Department of Chemistry and Beckman Institute for Advanced Science and Technology, University of Illinois, Urbana, IL 61801.

TC05 15 min 9:38

APPROXIMATE SCALING OF MATRIX ELEMENTS FOR MULTIDIMENSIONAL ANHARMONIC VIBRATIONAL POTENTIALS

DANE MADSEN AND MARTIN GRUEBELE, School of Chemical Sciences and Beckman Institute for Advanced Science and Technology, University of Illinois, Urbana, IL 61801.

TC06 15 min 9:55

A "MULTI-MOLECULE" RITZ PROGRAM

GIOVANNI MORUZZI, Dipartimento di Fisica dell'Università di Pisa, Piazza Torricelli 2, I-56126 Pisa, Italy.

Intermission

TC07

15 min 10:25

PATTERN RECOGNITION BY EXTENDED AUTO- AND CROSS-CORRELATION

STEPHEN L. COY, MATTHEW P. JACOBSON, and ROBERT W. FIELD, *Department of Chemistry, Massachusetts Institute of Technology, Cambridge, MA 02139.*

TC08

15 min 10:42

THE COMPUTATION OF ROTATIONAL AND VIBRATIONAL SPECTRUM OF VAN DER WAALS MOLECULES ON CRAY-T3D

X. T. WU, P. KORAMBATH, E. F. HAYES, *Dept. of Chemistry, The Ohio State University, Columbus, OH 43210*; ZDENKO TOMAŠIĆ, and DANNY SORESENSEN, *Dept. of Mathematical Sciences, Rice University, Houston, TX 77251.*

TC09

15 min 10:59

A SEMIEMPIRICAL PES FOR Kr-HS

PRAKASHAN P. KORAMBATH, X. T. WU, E. F. HAYES, C. C. CARTER and TERRY A. MILLER, *Dept. of Chemistry, The Ohio State University, Columbus, OH 43210.*

TC10

10 min 11:16

ANALYSES OF VIBRATIONS OF Ar_n AND Ar_nCO_2 CLUSTERS BY MOLECULAR DYNAMICS CALCULATION

Y. OZAKI, *Department of Chemistry, Faculty of Science, Josai University, Sakado, Saitama 350-02, Japan*; M. ICHIHASHI, T. KONDOW, *Department of Chemistry, School of Science, The University of Tokyo, Bunkyo-ku, Tokyo 113, Japan*; and K. KUCHITSU, *Department of Chemistry, Faculty of Science, Josai University, Sakado, Saitama 350-02, Japan.*

TC11

15 min 11:28

AB INITIO VIBRATIONAL SPLITTINGS FOR HYDROGEN ATOM TRANSFER IN $\text{HO}_2^-/\text{O}_2\text{H}^-$ ISOMERIZATION

WAI-TO CHAN and IAN P. HAMILTON, *Department of Chemistry, Wilfrid Laurier University, Waterloo, Ontario.*

TC12

15 min 11:45

AB INITIO STRUCTURES, VIBRATIONS, AND THERMOCHEMISTRY OF IO , IO^- , AND IO^+

P. HASSANZADEH^a and K. K. IRIKURA, *Physical and Chemical Properties Division, National Institute of Standard and Technology, Gaithersburg, MD 20899.*

^aGuest Researcher

TD. MICROWAVE
TUESDAY, JUNE 11, 1996 – 8:30 AM
Room: 1008 EVANS LAB

Chair: TERUHIKO OGATA, Shizuoka University, Shizuoka, Japan
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TD01 **15 min 8:30**

THE STRUCTURE OF HALOGEN DIMERS: MICROWAVE SPECTRUM OF (ClF)₂

K. HIGGINS, W. KLEMPERER, *Department of Chemistry, Harvard University, Cambridge, MA 02138*; F.-M. TAO, *Department of Chemistry, California State University, Fullerton, CA 92634*; E. ARUNAN, *Department of Chemistry, Indian Institute of Technology, Kanpur 208016, India*; T. EMILSSON, H.S. GUTOWSKY, *Department of Chemistry, University of Illinois, Urbana IL 61801*.

TD02 **15 min 8:47**

THE INTERMOLECULAR POTENTIAL SURFACE OF INERT GAS HALOGEN COMPLEXES AS PROBED BY HeClF

K. HIGGINS, W. KLEMPERER, *Department of Chemistry, Harvard University, Cambridge, MA 02138*; F.-M. TAO, *Department of Chemistry, California State University, Fullerton, CA 92634*.

TD03 **15 min 9:04**

FOURIER TRANSFORM MICROWAVE SPECTROSCOPY OF Ar-N₂O AND HCCH-N₂O

HELEN O. LEUNG, and DEEPA GANGWANI, *Department of Chemistry, Mount Holyoke College, South Hadley, MA 01075*.

TD04 **15 min 9:21**

DIRECT ABSORPTION OBSERVATION OF THE VAN DER WAALS BENDING BAND OF ArHCN BY MILLIMETERWAVE SPECTROSCOPY COMBINED WITH PULSED-JET EXPANSION TECHNIQUE. EXTENSION TO THE j=2-1 HOT BAND

KEIICHI TANAKA, KEISUKE UEMURA, and MITSUAKI SHIRASAKA, *Department of Chemistry, Faculty of Science, Kyushu University 33, Hakozaki, Higashiku Fukuoka 812-81, Japan*.

TD05 **10 min 9:38**

THE MICROWAVE SPECTRUM AND STRUCTURE OF THE CARBON DIOXIDE-SULFUR DIOXIDE COMPLEX

L. SUN, I. I. IOANNOU, and R. L. KUCZKOWSKI, *Department of Chemistry, The University of Michigan, Ann Arbor, MI 48109-1055*.

TD06 **15 min 9:50**

MICROWAVE SPECTRUM AND STRUCTURE OF HNO₃-H₂O

M. CANAGARATNA, J. A. PHILLIPS, M. OTT, and K. R. LEOPOLD, *Department of Chemistry, University of Minnesota, Minneapolis, MN 55455*.

Intermission

TD07 15 min 10:20

GAS PHASE STRUCTURE OF A FRIEDEL-CRAFTS INTERMEDIATE: MICROWAVE SPECTRUM OF $\text{CH}_3\text{F}\cdot\text{BF}_3$

J. A. PHILLIPS, M. CANAGARATNA, M. OTT, and K. R. LEOPOLD, *Department of Chemistry, University of Minnesota, Minneapolis, MN 55455.*

TD08 15 min 10:37

THE ROTATIONAL SPECTRUM OF ARGON-SILANE

Y. KAWASHIMA, *Department of Chemical Technology, Kanagawa Institute of Technology, Atsugi, Kanagawa 243-02, Japan*; R. D. SUENRAM, G. T. FRASER, and F. J. LOVAS, *Optical Technology Division, National Institute of Standards and Technology, Gaithersburg, MD 20899*; E. HIROTA, *The Graduate University for Advanced Studies, Hayama, Kanagawa, 240-01, Japan.*

TD09 15 min 10:54

MICROWAVE SPECTRUM OF THE Xe-PROPYLENE VAN DER WAALS COMPLEX

Th. BRUPBACHER, W. JÄGER^a, M. C. L. GERRY, *Department of Chemistry, University of British Columbia, Vancouver, B.C., V6T 1Z1, Canada*; D. F. EGGERS, *Department of Chemistry, University of Washington, Seattle, WA 98195, U. S. A..*

^aPresent address: Department of Chemistry, University of Alberta, Edmonton, Alta., Canada, T6G 2G2

TD10 15 min 11:11

FOURIER TRANSFORM MICROWAVE SPECTROSCOPY OF ARGON CYCLOBUTANONE

MICHAELEEN R. MUNROW, WEI CHEN, WALLACE C. PRINGLE, and STEWART E. NOVICK, *Department of Chemistry, Wesleyan University, Middletown, CT 06459.*

TD11 15 min 11:28

ROTATIONAL SPECTRA OF $\text{CH}_3\text{CCH}\cdot\text{NH}_3$, $\text{NCCCH}\cdot\text{NH}_3$, AND $\text{NCCCH}\cdot\text{OH}_2$

A. R. HIGHT WALKER, R. OMRON, G. T. FRASER, R. D. SUENRAM, *Optical Technology Division, National Institute of Standards and Technology, Gaithersburg, MD 20899*; G. HILPERT, *Institut für Angewandte Physik, Universität Bonn, Wegelerstraße 8, D-53115 Bonn, Germany.*

TD12 15 min 11:45

FOURIER TRANSFORM MICROWAVE SPECTROSCOPY OF TRIMETHYLENE SULFIDE MONOMER AND ARGON VAN DER WAALS COMPLEX IN THE RING-PUCKERING GROUND INVERSION STATES

W. C. PRINGLE, M. R. MUNROW, W. D. R. PREMASIRI, D. W. MCCAMANT, WEI CHEN, S. E. NOVICK, *Department of Chemistry, Wesleyan University, Middletown CT 06459.*

TE. SYMPOSIUM: ABSORPTION SPECTROSCOPY

TUESDAY, JUNE 11, 1996 – 1:30 PM

Room: 1153 SMITH LAB

Chair: KEVIN LEHMANN, Princeton University, Princeton, New Jersey

TE01 **INVITED TALK** **30 min 1:30**
TOWARDS THE ULTIMATE OPTICAL DETECTION SENSITIVITY: NEW SPECTROSCOPIC OPPORTUNITIES -
AND A ZILLION NEW WAVELENGTH/FREQUENCY STANDARDS

JOHN HALL, *JILA, NIST & Dept of Chemistry & Biochemistry, Univ. of Colorado, Boulder, CO 80309.*

TE02 **10 min 2:05**
NEW NEAR-INFRARED TRANSIENT ABSORPTION TECHNIQUES

BOR-CHEN CHANG and TREVOR J. SEARS, *Department of Chemistry, Brookhaven National Laboratory, Upton, NY 11973-5000.*

TE03 **15 min 2:17**
TRANSIENT FM SPECTROSCOPY FOR DOPPLER MEASUREMENTS OF PHOTOFRAGMENT VELOCITIES AND
VECTOR CORRELATIONS

SIMON W. NORTH, and GREGORY E. HALL, *Department of Chemistry, Brookhaven National Laboratory, Upton, NY 11973-5000.*

TE04 **10 min 2:34**
THEORETICAL AND EXPERIMENTAL ADVANTAGES OF A COMPACT MIRAGE SPECTROSCOPY SETUP FOR
TRACE GAS DETECTION

B. ZIMERING and A.C. BOCCARA, *CNRS UPR A0005, Laboratoire d'Optique Physique, ESCPI, 10, rue Vauquelin, Paris 75005, France.*

TE05 **15 min 2:46**
INTRACAVITY LASER ABSORPTION SPECTROSCOPY IN HIGHLY EXCITED OVERTONES OF HOCl: DENSITY
OF STATES, INTRAMOLECULAR ENERGY REDISTRIBUTION, AND LIFETIMES

A. KACHANOV, *Laboratoire de Spectrométrie Physique Université J. Fourier/CNRS/Grenoble BP87 38402 Saint Martin d'Hères Cedex France*; B. ABEL, A. CHARVAT, H. HAMANN, S. A. KOVALENKO, and J. TROE, *Institut für Physikalische Chemie der Universität Göttingen, Tammannstr.6, 37077 Göttingen.*

TE06 **10 min 3:03**
EXCITED STATE GAS PHASE SPECIES OBSERVED IN RADIOFREQUENCY PLASMAS STUDIED BY OPTICAL
EMISSION AND INTRACAVITY LASER SPECTROSCOPY TECHNIQUES

DEAN R. PETERMAN and JAMES J. O'BRIEN, *Department of Chemistry and Center for Molecular Electronics, University of Missouri-St. Louis, St. Louis, MO 63121-4499.*

TE07

15 min 3:15

EXPERIMENTAL STUDY OF ATOM FLUORESCENCE LINES IN THE LASER PRODUCED PLASMA

O. A. BUKIN, E. A. SVIRIDENKOV, *Lebedev Physical Institute, 53 Leninskii pr., Moscow Russia*; N. V. SUSHILOV and A. Yu. MAJOR, *Pacific Oceanological Institute, Russian Academy of Sciences, 43 Baltiyskaya, Vladivostok, 690041 Russia*.

TE'. ELECTRONIC (SMALL)**TUESDAY, JUNE 11, 1996 - 3:45 PM****Room: 1153 SMITH LAB****Chair: GEOFFREY DUXBURY, JILA, Boulder, Colorado****TE'01****10 min 3:45****FOURIER TRANSFORM EMISSION SPECTROSCOPY OF THE $A^2\Sigma^+-X^2\Pi$ TRANSITION OF SILVER MONOXIDE**

M. K. SIEBER and L. C. O'BRIEN, *Department of Chemistry, Southern Illinois University at Edwardsville, Edwardsville, IL 62026-1652.*

TE'02**10 min 3:57****EMISSION SPECTROSCOPY OF METAL FLUORIDES: NaF AND TiF**

ALEXANDRINA MUNTIANU, P. F. BERNATH, *Center for Molecular Beams and Laser Chemistry, University Waterloo, Waterloo, On., Canada, N2L 3G1*; R. S. RAM, *Department of Chemistry, University of Arizona, Tucson, AZ 85721*; S. P. DAVIS, *Department of Physics, University of California, Berkeley, CA 94720.*

TE'03**10 min 4:09****FOURIER TRANSFORM INFRARED EMISSION SPECTROSCOPY OF THE NEW $b^1\Pi-a^1\Sigma^+$ TRANSITION OF BN**

R. S. RAM, *Department of Chemistry, University of Arizona, Tucson, AZ 85721*; P. F. BERNATH, *Department of Chemistry, University of Waterloo, Waterloo, Ontario, Canada N2L 3G1.*

TE'04**15 min 4:21****CHARACTERISATION OF SEVERAL ELECTRONIC STATES OF FeH.**

DAMIAN M. GOODRIDGE, DANIEL F. HULLAH, AND JOHN M. BROWN, *The Physical and Theoretical Chemistry Laboratory, South Parks Road, Oxford, UK, OX1 3QZ.*

TE'05**15 min 4:38****ELECTRONIC SPECTROSCOPY OF RhH AND RhD IN THE 430 - 470 nm REGION**

JIANYING CAO, WALTER J. BALFOUR, AND CHARLES X. W. QIAN, *Department of Chemistry, University of Victoria, P.O.Box 3065, Victoria, B.C., Canada, V8W 3P6.*

TE'06**15 min 4:55****LASER INDUCED FLUORESCENCE SPECTRUM OF THE $A^2\Pi-X^2\Sigma$ TRANSITION OF ZrN**

C. M-T. CHAN, HAIYANG LI AND A. S-C. CHEUNG, *Department of Chemistry, The University of Hong Kong, Pokulam Road, Hong Kong.*

TE'07**10 min 5:12****LASER ABSORPTION SPECTROSCOPY OF LaF^{+} : ACCURATE TERM ENERGIES FOR THE $H^2\Pi$, $D^2\Phi$, AND $X^2\Delta$ STATES**

L. A. KALEDIN, A. L. KALEDIN, AND M. C. HEAVEN, *Department of Chemistry, Emory University, Atlanta, GA 30322.*

TE'08

5 min 5:24

LASER ABSORPTION SPECTROSCOPY OF LaF: ANALYSIS OF THE $B^1\Pi-X^1\Sigma^+$ TRANSITION

L. A. KALÉDIN, A. L. KALÉDIN, and M. C. HEAVEN, *Department of Chemistry, Emory University, Atlanta, GA 30322.*

TE'09

15 min 5:31

ELECTRONIC SPECTROSCOPY OF RuC FROM 12,000 TO 19,000 CM^{-1}

J. D. LANGENBERG, R. DABELL, D. DREESSEN, and M. C. MORSE, *Department of Chemistry, University of Utah, Salt Lake City, UT 84112.*

TF. RADICALS

TUESDAY, JUNE 11, 1996 – 1:30 PM

Room: 1009 SMITH LAB

Chair: TAKAYOSHI AMANO, Ibaraki University, Mito, Japan

TF01

15 min 1:30

RENNER-TELLER CORRELATION DIAGRAMS FOR ORBITAL ANGULAR MOMENTUM IN Π AND Δ STATES OF TRIATOMIC MOLECULES

G. DUXBURY^c, B. D. MCDONALD, *Department of Physics and Applied Physics, Strathclyde University, Glasgow G4 0NG, Scotland, U.K.*; A. ALJAH, *Facultät für Chemie, Universität Bielefeld, D-4800 Bielefeld, Germany.*

^cvisiting fellow at JILA

TF02

15 min 1:47

FERMI RESONANCE PERTURBATIONS OF ORBITAL ANGULAR MOMENTUM (RENNER-TELLER) COUPLING IN TRIATOMIC MOLECULES: THE STRETCH-BENDER APPROACH

G. DUXBURY^d, B. D. MCDONALD, *Department of Physics and Applied Physics, Strathclyde University, Glasgow G4 0NG, Scotland, U.K.*; Ch. JUNGEN, *Laboratoire Aimée Cotton de CNRS, Université de Paris-Sud, 91405 Orsay CEDEX, FRANCE*; A. ALJAH, *Facultät für Chemie, Universität Bielefeld, D-4800 Bielefeld, Germany.*

^dvisiting fellow at JILA

TF03

15 min 2:04

THE ULTRA VIOLET SPECTRUM OF THE NCN RADICAL

S. A. BEATON, J. M. BROWN, *Physical and Theoretical Chemistry Laboratory, South Parks Road, Oxford, UK, OX1 3QZ*; Y. ITO, *Department of Mechanical Engineering, Nagaoka University of Technology, 1603-1 Kamitomioka, Nagaoka, Niigata 940-21, Japan.*

TF04

15 min 2:21

HIGH RESOLUTION LIF SPECTROSCOPY OF THE MgNC RADICAL.

ROSSANA RUBINO, CHRISTOPHER C. CARTER, JAMES M. WILLIAMSON, DAVID E. POWERS, and TERRY A. MILLER, *Laser Spectroscopy Facility, Department of Chemistry, The Ohio State University, Columbus, OH 43210.*

TF05

15 min 2:38

OPTICAL SPECTROSCOPY OF THE NIOBIUM METHYLIDYNE FREE RADICAL, NbCH

DAVID A. GILLET, M. BARNES, G. F. METHA^a, K. ATHANASSENAS and A. J. MERER, *Department of Chemistry, University of British Columbia, 2036 Main Mall, Vancouver, B.C. V6T 1Z1, Canada.*

^aPresent address: School of Chemistry, University of Sydney, Building F11, Sydney, N.S.W. 2006, Australia

TF06

15 min 2:55

THE ELECTRONIC SPECTRUM OF TANTALUM METHYLIDYNE, TaCH

M. BARNES, DAVID A. GILLETT, G. F. METHA^a, K. ATHANASSENAS and A.J. MERER, *Department of Chemistry, University of British Columbia, 2036 Main Mall, Vancouver, B.C. V6T 1Z1, Canada.*

^aPresent address: School of Chemistry, University of Sydney, Building F11, Sydney, N.S.W. 2006, Australia

TF07

15 min 3:12

A MOLECULAR BEAM OPTICAL STUDY OF YCC

J. XIN, A. J. MARR and T. C. STEIMLE, *Department of Chemistry and Biochemistry, Arizona State University, Tempe, AZ, 85287-1604.*

TF08

15 min 3:29

THE OPTICAL AND OPTICAL/STARK SPECTRUM OF IRIDIUM MONOCARBIDE AND MONONITRIDE

A. J. MARR, M. E. FLORES and T. C. STEIMLE, *Dept. of Chemistry and Biochemistry, Arizona State University, Tempe, AZ 85287-1604.*

Intermission

TF09

15 min 4:00

A NEW DISCHARGE NOZZLE FOR SPECTROSCOPIC STUDIES IN SUPERSONIC JETS

ANDREW J. BEZANT, DANIEL D. TURNER, GUY DORMER, and ANDREW M. ELLIS, *Department of Chemistry, University of Leicester, University Road, Leicester LE1 7RH, UK.*

TF10

15 min 4:17

SPECTROSCOPY AND EXCITED STATE DYNAMICS OF BORON ATOM-RARE GAS AND B-H₂ VAN DER WAALS COMPLEXES

XIN YANG and PAUL J. DAGDIGIAN, *Department of Chemistry, The Johns Hopkins University, Baltimore, MD 21218-2685.*

TF11

15 min 4:34

VIBRATIONAL SPECTROSCOPY OF Rg•SH COMPLEXES

CHRISTOPHER C. CARTER, MIN-CHIEH YANG, TERRY A. MILLER, *The Ohio State University, Department of Chemistry, The Laser Spectroscopy Facility, 120 West 18th Ave., Columbus, OH 43210.*

TF12

15 min 4:51

ELECTRONIC PREDISSOCIATION DYNAMICS OF CN(A)-Ne

W. G. LAWRENCE AND M. C. HEAVEN, *Department of Chemistry, Emory University, Atlanta, GA 30322.*

TF13

15 min 5:08

AXIS SWITCHING IN THE \tilde{B}^2A' TRANSITION OF HCO AND FLUORESCENCE LIFETIMES OF THE $\tilde{B}^2A'(0,0,0)$ ROTATIONAL STATES

SHIH-HUANG LEE and I-CHIA CHEN, *Department of Chemistry, National Tsing Hua University, Hsinchu, Taiwan 30043, Republic of China.*

TF14

10 min 5:25

ROTATIONALLY RESOLVED LIF SPECTRA OF JET-COOLED HCCS RADICAL

JAMES M. WILLIAMSON, CHRISTOPHER C. CARTER, DAVID E. POWERS, ROSSANA RUBINO, AND TERRY A. MILLER, *The Ohio State University, Department of Chemistry, The Laser Spectroscopy Facility, 120 West 18th Ave., Columbus, OH 43210.*

TF15

10 min 5:37

ROTATIONALLY RESOLVED NEAR-INFRARED SPECTRUM OF HCB_r

BOR-CHEN CHANG, and TREVOR J. SEARS, *Department of Chemistry, Brookhaven National Laboratory, Upton, NY 11973-5000.*

TF16

10 min 5:49

THE PRODUCTION OF RADICAL SPECIES BY A HIGH TEMPERATURE NOZZLE IN A FREE JET EXPANSION: THE STUDY OF CF₂ AND CFB_r BY LASER INDUCED FLUORESCENCE

MELANIE R. CAMERON, PAMELA. T. KNEPP and SCOTT. H. KABLE, *Department of Physical Chemistry, University of Sydney, Sydney, NSW, AUSTRALIA, 2006.*

TG. JET AND BEAM

TUESDAY, JUNE 11, 1996 – 1:30 PM

Room: 1005 SMITH LAB

Chair: DAVID PERRY, University of Akron, Akron, Ohio
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TG01 15 min 1:30
 RESONANT ION DIP INFRARED SPECTROSCOPY (RIDIRS) OF BENZENE-(METHANOL)_m HYDROGEN-BONDED CLUSTERS

R. N. PRIBBLE, F. C. HAGEMEISTER, AND T. S. ZWIER, *Department of Chemistry, Purdue University, West Lafayette, IN 47907-1393.*

TG02 15 min 1:47
 ROTATIONALLY RESOLVED VIBRATIONAL OVERTONE SPECTRA OF JET-COOLED METHANOL

OLEG V. BOYARKIN, LUCIA LUBICH, THOMAS R. RIZZO, *Laboratoire de chimie physique moléculaire, Ecole Polytechnique Fédérale de Lausanne, CH- Ecublens, 1015 Lausanne, Switzerland;* and DAVID S. PERRY, *Department of Chemistry, University of Akron, Akron, Ohio, 44325.*

TG03 15 min 2:04
 JET-COOLED INFRARED SPECTRA AND INVESTIGATION OF THE TORSION-ROTATION ENERGY LEVELS OF METHANOL IN THE C-H STRETCH REGION

LI-HONG XU, *Department of Physical Sciences, University of New Brunswick, Saint John, N.B., Canada E2L 4L5;* X. WANG, D. S. PERRY, *Department of Chemistry, University of Akron, Akron, OH 44325-3601;* G. T. FRASER and A. S. PINE, *Radiometric Physics Division, National Institute of Standards and Technology, Gaithersburg, MD 20899.*

TG04 10 min 2:21
 JET-COOLED INFRARED SPECTRUM OF THE ν_6 BAND OF CH₂F₂

THOMAS J. CRONIN, XIAOLIANG WANG, AND DAVID S. PERRY, *Department of Chemistry, The University of Akron, Akron, OH 44325-3601;* GREGORY A. BETHARDY, *Chemistry Division, Argonne National Laboratory, Argonne, IL 60439.*

TG05 15 min 2:33
 MBER SPECTROSCOPY OF ISOCYANIC ACID (HNCO)

BRIAN MEEHAN, and J. S. MUENTER, *Department of Chemistry, University of Rochester, Rochester, NY 14627.*

TG06 15 min 2:50
 THE MICROWAVE SPECTRUM OF A MOLECULAR EIGENSTATE I

BROOKS H. PATE, *Department of Chemistry, University of Virginia, Charlottesville, VA 22901.*

TG07

15 min 3:07

THE MICROWAVE SPECTRUM OF A MOLECULAR EIGENSTATE II

BROOKS H. PATE, CHUNG YI LEE, *Department of Chemistry, University of Virginia, Charlottesville, VA 22901.*

Intermission

TG08

15 min 3:40

EIGENSTATE RESOLVED INFRARED SPECTROSCOPY OF 1,1,1-d₃-ETHANE IN THE REGION AROUND 5900 CM⁻¹

J. W. DOLCE, A. CALLEGARI, H. K. SRIVASTAVA, K. K. LEHMANN, and G. SCOLES, *Princeton University, Department of Chemistry, Princeton, NJ, 08544.*

TG09

15 min 3:57

EIGENSTATE RESOLVED INFRARED AND MILLIMETER WAVE - INFRARED DOUBLE RESONANCE STUDY OF METHYLAMINE IN THE N-H STRETCH OVERTONE REGION

H. K. SRIVASTAVA, A. CALLEGARI, K. K. LEHMANN, G. SCOLES, *Princeton University, Department of Chemistry, Princeton, NJ, 08544*; U. MERKER^e, *University of Bonn, Institut für Angewandte Physik, Wegelerstr. 8, 53115 Bonn, Germany.*

^eSupported by the German Academic Exchange Service (DAAD)

TG10

15 min 4:14

EIGENSTATE RESOLVED INFRARED AND INFRARED-INFRARED DOUBLE RESONANCE STUDY OF BENZENE VIBRATIONAL RELAXATION IN THE C-H STRETCH FIRST OVERTONE REGION

A. CALLEGARI, H. K. SRIVASTAVA, K. K. LEHMANN, G. SCOLES, *Princeton University, Department of Chemistry, Princeton, NJ, 08544*; U. MERKER^f, *University of Bonn, Institut für Angewandte Physik, Wegelerstr. 8, 53115 Bonn, Germany.*

^fSupported by the German Academic Exchange Service (DAAD)

TG11

10 min 4:31

MOLECULAR BEAM INFRARED SPECTRUM OF THE FIRST C-H STRETCHING OVERTONE REGION OF NITROMETHANE

M. HALONEN^a, L. HALONEN^a, K. K. LEHMANN AND A. CALLEGARI, *Department of Chemistry, Princeton University, NJ 08544.*

^aPermanent address of M. and L. Halonen: Laboratory of Physical Chemistry, P.O. Box 55 (A.I. Virtasen aukio 1), FIN-00014 University of Helsinki, Finland

TG12

5 min 4:43

INFRARED SPECTRA OF METHYLAMINE IN THE ASYMMETRIC C-H STRETCH REGION

ANDREI V. CHIROKOLAVA, THOMAS J. CRONIN, XIAOLIANG WANG, C. MICHAEL LINDSAY, and DAVID S. PERRY, *Department of Chemistry, The University of Akron, Akron, OH 44325-3601.*

TG13

15 min 4:50

INFRARED DIODE-LASER MOLECULAR BEAM SPECTRUM OF THE ν_2 BAND OF ClONO₂ AT 1293 CM⁻¹

J. L. DOMENECH, *Instituto de Estructura de la Materia, CSIC, Serrano 119, 28006 Madrid, Spain*; J. -M. FLAUD, *LPMA, Université P. et M. Curie, 4, Place Jussieu 75252 Paris Cedex 05, France*; G. T. FRASER, A. M. ANDREWS, W. J. LAFFERTY, *Optical Technology Division, NIST, Gaithersburg, MD 20899*; P. L. WATSON, *Dupont Central Research and Development, Experimental Station E328/315, P. O. Box 80328, Wilmington DE 19880-0328*.

TG14

15 min 5:07

THE $\nu_7 + \nu_9 - \nu_9$ HOT BAND IN ETHANE

W. LEO MEERTS, JOS OOMENS, and JÖRG REUSS, *Department of Molecular and Laser Physics, Catholic University of Nijmegen, Toernooiveld 1, 6525ED Nijmegen, The Netherlands*.

TG15

15 min 5:24

HIGH-RESOLUTION MICROWAVE AND INFRARED MOLECULAR-BEAM STUDIES OF THE CONFORMERS OF 1,1,2,2-TETRAFLUOROETHANE

S. C. STONE, L. A. PHILIPS, *Department of Chemistry, Cornell University, Ithaca, NY 14853*; G. T. FRASER, F. J. LOVAS, L. -H. XU, *Optical Technology Division, National Institute of Standards and Technology, Gaithersburg, MD 20899*; S. W. SHARPE, *Molecular Sciences Research Center, Pacific Northwest Laboratory, Richland, WA 99352*.

TH. MATRIX AND CONDENSED PHASE

TUESDAY, JUNE 11, 1996 - 1:30 PM

Room: 1008 EVANS LAB

Chair: BRUCE AULT, University of Cincinnati, Cincinnati, Ohio

TH01 15 min 1:30
ISOMERS OF SO₂: INFRARED ABSORPTION OF SOO IN SOLID AR

YUAN-PERN LEE, LI-SHUN CHEN, *Department of Chemistry, National Tsing Hua University, Hsinchu, TAIWAN 30043.*

TH02 15 min 1:47
MATRIX ISOLATION SPECTROSCOPY OF Cl₃

W. G. LAWRENCE, R. FULGHUM, and M. C. HEAVEN, *Department of Chemistry, Emory University, Atlanta, GA 30322.*

TH03 15 min 2:04
INFRARED SPECTROSCOPIC EVIDENCE FOR THE YLIDION (H₂CXH⁺) ISOMERS OF THE METHYL HALIDES TRAPPED IN SOLID NEON

CATHERINE L. LUGEZ, DANIEL FORNEY MARILYN E. JACOX, and KARL K. IRIKURA, *National Institute of Standards and Technology, Gaithersburg, MD 20899.*

TH04 15 min 2:21
SPECTROSCOPY OF CARBON CLUSTER ANIONS IN ARGON MATRICES

J. SZCZEPANSKI, S. EKERN, and M. VALA, *Department of Chemistry and The Center for Chemical Physics, University of Florida, Gainesville, FL 32611.*

TH05 15 min 2:38
THEORETICAL STUDIES OF THE C₃H₂O POTENTIAL SURFACE: A MECHANISM FOR PROPYNAL FORMATION AND DEPLETION

S. P. EKERN, J. SZCZEPANSKI, and M. VALA, *Department of Chemistry and The Center for Chemical Physics, University of Florida, Gainesville, FL 32611.*

TH06 15 min 2:55
LOW TEMPERATURE MATRIX ISOLATION STUDIES OF BORON TRIAZIDE

CHRISTOPHER J. LINNEN, JULANNA V. GILBERT, *Department of Chemistry, University of Denver, Denver, CO 80208.*

TH07 15 min 3:12
INFRARED SPECTRUM OF O₃⁻ ISOLATED IN SOLID NEON AND EVIDENCE FOR THE STABILIZATION OF O₂ ··· O₄⁺

CATHERINE L. LUGEZ, WARREN E. THOMPSON, and MARILYN E. JACOX, *Molecular Physics Division, National Institute of Standards and Technology, Gaithersburg, MD 20899.*

Intermission

TH08 **15 min 3:45**

LOW TEMPERATURE SPECTROSCOPY AND ASTROPHYSICAL ISSUES. THE INTERSTELLAR EXTINCTION

F. SALAMA, *NASA-Ames Research Center, MS 245-6, Moffett Field, CA 94035.*

TH09 **15 min 4:02**

ELECTRONIC ABSORPTION SPECTROSCOPY OF MATRIX ISOLATED POLYCYCLIC AROMATIC HYDROCARBON IONS. CONTRIBUTION TO ASTROPHYSICAL ISSUES

F. SALAMA, *NASA-Ames Research Center, MS 245-6, Moffett Field, CA 94035.*

TH10 **15 min 4:19**

THE PHOTOLYSIS OF ACETYLENE HALIDES REACTION WITH OXYGEN

MEI-LEE HWANG, *Department of Chemical Engineering, Kaohsiung Polytechnic Institute, Taiwan, 84008;*
YU-PING KUO, *Department of Applied Chemistry, Chia Nan Junior College of Pharmacy, Taiwan.*

TH11 **10 min 4:36**

PHOTOCHEMISTRY OF MATRIX-ISOLATED TRIFLUORONITROSOMETHANE (CF₃NO)

MEGAN MORGAN and C. A. BAUMANN, *Department of Chemistry, University of Scranton, Scranton, PA 18510.*

TH12 **15 min 4:48**

EXPERIMENTAL MATRIX ISOLATION AND THEORETICAL AB INITIO STUDIES OF VIBRATIONAL SPECTRA OF HYDROGEN HALIDE COMPLEXES WITH STRONG NITROGEN BASES

KRYSTYNA SZCZEPANIAK, WILLIS B. PERSON, *Department of Chemistry, University of Florida, Gainesville, FL 32611;* JANET E. DEL BENE, *Department of Chemistry, Youngstown State University, Youngstown, OH 44555.*

TH13 **15 min 5:05**

INFRARED MATRIX ISOLATION STUDY OF THE REACTION OF TiCl₄ WITH LEWIS ACIDS; SPECTROSCOPIC CHARACTERIZATION OF Cl₃TiOCH₃

BRUCE S. AULT and JENNIFER B. EVERHART, *Department of Chemistry, University of Cincinnati, P. O. Box 210172, Cincinnati, OH 45221-0172.*

TH14 **15 min 5:22**

MAGNETO-IR SPECTRA OF MATRIX-ISOLATED NiH AND NiH₂ MOLECULES AND THEORETICAL CALCULATIONS OF THE LOWEST ELECTRONIC STATES OF NiH₂

S. LI, R. J. VAN ZEE, W. WELTNER, JR., M. G. CORY, and M. C. ZERNER, *Department of Chemistry and Quantum Theory Project, University of Florida, Gainesville, FL 32611.*

TH15**10 min 5:39**

REACTIONS OF LASER ABLATED Be ATOMS WITH H₂O: INFRARED SPECTRA OF HOBeOH AND H₂O-BeO IN SOLID ARGON.

C. THOMPSON^a and L. ANDREWS, *University of Virginia, Dept. of Chemistry, McCormick Road, Charlottesville, VA 22901.*

^aCurrently a National Research Council-Naval Research Laboratory Associate. Naval Research Laboratory. Code 6110 4555 Overlook Avenue SW Washington DC 20375-5342.

TH16**10 min 5:51**

MATRIX INFRARED AND UV-VIS. STUDY OF REACTION BETWEEN Mg AND CH₃X; X=Br, Cl

V. N. SOLOV'EV, A. V. NEMUKHIN, G. B. SERGEEV, *Chemistry Department, Moscow State University, 119899, Moscow Russia.*

WA. PLENARY SESSION**WEDNESDAY, JUNE 12, 1996 – 8:45 AM****Room: AUDITORIUM INDEPENDENCE HALL**

Chair: MATTHEW PLATZ, The Ohio State University, Columbus, Ohio
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WA01**40 min 8:45****ROTATIONAL SPECTROSCOPY OF PRE-REACTIVE MULLIKEN COMPLEXES OF HALOGENS WITH LEWIS BASES.**

A. C. LEGON, *Department of Chemistry, University of Exeter, Stocker Road, Exeter, EX4 4QD, UK.*

WA02**40 min 9:30****RECENT RESULTS ON HYDROGEN PEROXIDE AND NITRIC ACID**

A. PERRIN, *Laboratoire de Physique Moléculaire et Applications, C.N.R.S., Université Pierre et Marie Curie, Case Courrier 76, Tour 13, 4, Place Jussieu, F-75252 Paris Cedex 05, France.*

Intermission**WA03****40 min 10:30****STRUCTURE AND DYNAMICS OF LARGE MOLECULES AND THEIR VAN DER WAALS COMPLEXES BY HIGH RESOLUTION UV LASER SPECTROSCOPY**

W. LEO MEERTS, *Department of Molecular and Laser Physics, University of Nijmegen, P.O. Box 9010, 6500 GL Nijmegen, The Netherlands.*

WA04**40 min 11:15****HIGH-RESOLUTION SPECTROSCOPY OF SINGLE MOLECULES IN SOLIDS**

W. E. MOERNER, *Department of Chemistry and Biochemistry, University of California at San Diego, La Jolla, CA 92093-0340.*

WE. INFRARED

TUESDAY, JUNE 11, 1996 – 1:30 PM

Room: 1153 SMITH LAB

Chair: MARY-ANN SMITH, NASA/Langley Research Center, Hampton, Virginia

WE01

10 min 1:30

HIGH RESOLUTION ANALYSIS OF THE ν_2 , $2\nu_2$, $3\nu_2$, ν_1 AND ν_3 BAND OF HYDROGEN TELLURIDE

O. POLANZ, H. BÜRGER, *BUGH Wuppertal, FB 9 Anorganische Chemie, Gaußstr. 20, D-42097 Wuppertal, Germany*; J. -M. FLAUD, Ph. ARCAS, M. BETRENCOURT, *LPMA, CNRS, Université P. et M. Curie, 4, Place Jussieu, F-75252 Paris Cedex 05, France*; W. J. LAFFERTY, *Optical Technology Division, NIST, Gaithersburg, MD 20899*.

WE02

15 min 1:42

ANALYSIS OF THE FIRST AND SECOND TRIADS OF H₂S FROM 2200 TO 4100 CM⁻¹

L. R. BROWN, J. A. CRISP, D. CRISP, *Jet Propulsion Laboratory, California Institute of Technology, 4800 Oak Grove Drive, Pasadena, California 91109*; A. PERRIN, *Laboratoire de Physique Moléculaire Applications CNRS, Université Pierre et Marie Curie Bte 76, 4 Place Jussieu 75252 Paris Cedex 05, France*; A. D. BYKOV, O. V. NAUMENKO, M. A. SMIRNOV and L. N. SINITSIA, *Institute of Atmospheric Optics, SB, Russian Academy of Science, 634055, Tomsk, Russia*.

WE03

10 min 1:59

FOURIER TRANSFORM INFRARED SPECTRA OF FORMALDOXIME: THE ν_7 , ν_9 , ν_{11} , ν_{12} , AND $2\nu_{12}$, BANDS

G. DUXBURY^g, G. RITCHIE, *Department of Physics and Applied Physics, Strathclyde University, Glasgow G4 0NG, Scotland, UK*; R. A. BANNAI, *Department of Physics, University of Bahrain, P.O. Box: 32038, Bahrain*; S. KLEE, *Physikalisch-Chemisches Institute der Justus-Liebig Universität, D-6300 Giessen, Germany*.

^gvisiting fellow at JILA

WE04

15 min 2:11

LOW TEMPERATURE FTIR SPECTRA OF METHYL SILANE

CHANGHONG XIA, GEOFFREY DUXBURY^h, *Department of Physics and Applied Physics, Strathclyde University, Glasgow G4 0NG, Scotland, UK*; DAVID NEWNHAN, and JOHN BALLARD, *Atmospheric Science Division, Space Science Department, Rutherford Appleton Laboratory, Chilton, Didcot, OX11 0QX, UK*.

^hvisiting fellow at JILA

WE05

15 min 2:28

VIBRATIONALLY EXCITED HCl AND HF PRODUCED FROM PHOTODISSOCIATION OF CH₃CFCl₂ AT 193 NM BY MEANS OF TIME-RESOLVED FTIR

PEY-SHIUN YEH, YUAN-PERN LEE, *Department of Chemistry, National Tsing Hua University, Hsinchu, TAIWAN 30043*.

WE06

15 min 2:45

FTIR DETECTION OF P_4O_{10} FROM COMBUSTION OF ELEMENTAL PHOSPHORUS

R.C. MOWREY, C.H. DOUGLASSⁱ, B.A. WILLIAMS, and H.D. LADOUCEUR, *Chemistry Division, Code 6100, Naval Research Laboratory, Washington, DC 20375-5000.*

ⁱNova Research, Inc., 1900 Elkin Street, Suite 230, Alexandria, VA 22308

WE07

15 min 3:02

INTERACTION OF VIBRATIONAL FUNDAMENTAL AND COMBINATION STATES OF ETHYLENE IN 3 μm REGION

BORIS G. SARTAKOV, *General Physics Institute RAS, Vavilov str. 38, 117942, Moscow, Russia*; JOS OOMENS and JÖRG REUSS, *Department of Molecular and Laser Physics, Catholic University of Nijmegen Toernooiveld 1, 6525ED Nijmegen, The Netherlands.*

Intermission

WE08

15 min 3:40

THE CARBODIIMIDE SPECTRUM IN THE WAVENUMBER RANGE OF 450-1000 CM^{-1} AND IN THE THz REGION

W. JABS, J. KOPUT, M. WINNEWISSER, *Physikalisch-Chemisches Institut, Justus-Liebig-Universität, D-35392 Giessen, Germany*; S. P. BELOV, Th. KLAUS, and G. WINNEWISSER, *I. Physikalisches Institut, Universität zu Köln, D-50937 Köln, Germany.*

WE09

15 min 3:57

INFRARED EMISSION SPECTROSCOPY OF THE COINAGE METAL HYDRIDES AND DEUTERIDES

F. CHARRON, S. -K. LEE, and P. F. BERNATH, *Department of Chemistry, University of Waterloo, Waterloo, ON N2L 3G1.*

WE10

15 min 4:14

HIGH RESOLUTION INFRARED SPECTROSCOPY OF THE ν_5 AND ν_7 BANDS OF HEXAFLUOROETHANE

THOMAS A. BLAKE, STEVEN W. SHARPE, *Battelle/Pacific Northwest National Laboratory, P. O. Box 999, MS K3- 58, Richland, WA 99352*; STEVEN C. STONE, LAURA A. PHILIPS, *Department of Chemistry, Cornell University, Ithaca, NY 14853-1301.*

WE11

15 min 4:31

TORSION-VIBRATION INTERACTIONS IN THE CH_3 -ROCKING AND OH-BENDING FUNDAMENTALS OF C-13 METHANOL

ADRIANA PREDOI AND R.M. LEES, *Centre for Laser Applications and Molecular Science, Department of Physics, University of New Brunswick, Fredericton, N.B., Canada E3B 5A3.*

WE12

15 min 4:48

A COMPLETE STRUCTURE OF THE ANTIROTAMER OF 1,2-DIFLUOROETHANE FROM HIGH RESOLUTION INFRARED SPECTROSCOPY

NORMAN C. CRAIG, ANTHONY CHEN, and KI HWAN SUH, *Department of Chemistry, Oberlin College, Oberlin, OH 44074*; GEORG C. MELLAU, STEFAN KLEE, *Physikalisch-Chemisches Institut der Justus-Liebig-Universität, Heinrich Buff Ring 58, D-35392 Giessen, Germany*.

WE13

10 min 5:05

ANALYSIS OF A C-TYPE BAND OF TRANS-1,2-DICHLOROETHYLENE- $^{35}\text{Cl}_2$ IN NATURAL ABUNDANCE IN THE HIGH RESOLUTION INFRARED SPECTRUM

NORMAN C. CRAIG, EMILIO L. MORALES, *Department of Chemistry, Oberlin College, Oberlin, OH 44074*; GEORG C. MELLAU, and STEFAN KLEE, *Physikalisch-Chemisches Institut der Justus-Liebig-Universität, Heinrich Buff Ring 58, D-35392 Giessen, Germany*.

WE14

10 min 5:17

THE IR SPECTROSCOPY INVESTIGATION OF THE HYDRIDE-WATER INTERMOLECULAR INTERACTION IN LIQUID AND GASEOUS PHASES

P. SENNIKOV, V. SHKRUNIN, D. RALDUGIN, and V. CHORSHEV, *Institute of Chemistry of High-Purity Substances, Russian Academy of Sciences, Nizhny Novgorod, 603600 Russia*.

WE15

15 min 5:29

RAMAN STUDY OF MOLECULAR VIBRATIONAL RELAXATION IN H-BONDED SYSTEMS

V. POGORELOV, E. HODJIEVA, A. LIZENGEVICH, A. VINIUCHUK, *Department of Physics, Kiev Taras Shevchenko's University, Glushkov pr. 6, Kiev 252127, Ukraine*.

WE16

15 min 5:46

SPECTROSCOPIC EVALUATION OF THE STRUCTURE AND DYNAMICS OF THE HYDROGEN BONDS IN DIFFERENT CRYSTAL MODIFICATIONS OF POTASSIUM BIODATE

A.I.BARABASH, T.A.GAVRILKO, G.A.PUCHKOVSKAYA, I.V.SEKIRIN, *Institute of Physics, National Academy of Sciences of Ukraine, Prosp. Nauki, 46, 252650 Kiev, Ukraine*; J.BARAN AND H.RATAJCZAK, *Institute of Low Temperature and Structure Research, Polish Academy of Sciences, 2 Okolna Street, 50-950 Wroclaw, Poland*.

WF. MICROWAVE: RADICALS AND IONS

WEDNESDAY, JUNE 12, 1996 – 1:30 PM

Room: 1009 SMITH LAB

Chair: STEPHEN KUKOLICH, University of Arizona, Tucson, Arizona

WF01 15 min 1:30

STRUCTURE OF LiOH FROM MICROWAVE SPECTROSCOPY AND *AB INITIO* THEORY

A.J. APPONI, L.M. ZIURYS, *Department of Chemistry, Arizona State University, Tempe, AZ 85287*; F.-M. TAO, *Department of Chemistry, California State University, Fullerton, CA 92634*; K. HIGGINS, W. KLEMPERER, *Department of Chemistry, Harvard University, Cambridge, MA 02138*.

WF02 15 min 1:47

THE MILLIMETER/SUB-MM WAVE SPECTRUM OF THE FeCl RADICAL ($X^6\Delta_i$)

B.-Z. LI M. D. ALLEN, and L. M. ZIURYS, *Department of Chemistry and Biochemistry, Arizona State University, Tempe, Arizona 85287-1604*.

WF03 15 min 2:04

^{19}F SPIN-ROTATION CONSTANTS AND CHEMICAL SHIFTS OF UNSTABLE MOLECULES FROM THEIR MICROWAVE SPECTRA

BETHANY GATEHOUSE, HOLGER S. P. MÜLLER^a, and MICHAEL C. L. GERRY, *University of British Columbia, Department of Chemistry, 2036 Main Mall, Vancouver, B.C., Canada, V6T 1Z1*.

^apresent address: Jet Propulsion Laboratory, California Institute of Technology, Pasadena, California, 91109

WF04 15 min 2:21

THE PURE ROTATIONAL SPECTRUM OF MAGNESIUM SULFIDE PRODUCED BY LASER ABLATION

KALEY A. WALKER and MICHAEL C.L. GERRY, *Department of Chemistry, University of British Columbia, Vancouver, B.C., Canada, V6T 1Z1*.

WF05 15 min 2:38

ROTATIONAL SPECTRA OF JET-COOLED ION COMPLEXES

YASUHIRO OHSHIMA, *Department of Chemistry, Graduate School of Science, Kyoto University, Sakyo-ku, Kyoto 606-01, JAPAN*; YOSHIHIRO SUMIYOSHI, AND YASUKI ENDO, *Department of Pure and Applied Sciences, Faculty of Arts and Sciences, The University of Tokyo, Meguro-ku, Tokyo 153, JAPAN*.

WF06 15 min 2:55

NEW MEASUREMENTS OF THE PROTON MIGRATION TUNNELING SPLITTING IN THE ROTATIONAL SPECTRUM OF C_2H_3^+

M. CORDONNIER, *Laboratoire de Spectroscopie Hertzienne, U.F.R de Physique, Université des Sciences et Technologies de Lille, Bât. P5, Villeneuve d'Ascq, 59655, France*; L. H. COUDERT, *Laboratoire de Physique Moléculaire et Applications, C.N.R.S., Université Pierre et Marie Curie, Tour 13, 4, Place Jussieu, 75252 Paris, Cedex 05, France*.

WF07

15 min 3:12

INTERNAL ROTATION IN THE CH_5^+ MOLECULAR ION

ALLAN L. L. EAST, M. KOLBUSZEWSKI and P. R. BUNKER, *Steacie Institute for Molecular Sciences, National Research Council of Canada, Ottawa, Ontario, Canada K1A 0R6.*

WF08

15 min 3:29

OBSERVATION OF JET-COOLED RADICALS AND IONS BY MILLIMETERWAVE SPECTROSCOPY COMBINED WITH PULSED-JET EXPANSION AND DISCHARGE NOZZLE TECHNIQUE

KEIICHI TANAKA and KEISUKE UEMURA, *Department of Chemistry, Faculty of Science, Kyushu University 33, Hakozaki, Higashiku Fukuoka 812-81, Japan.*

Intermission

WF09

15 min 4:00

MILLIMETER-WAVE SPECTRUM OF SILENE: H_2CSiH_2

S. BAILLEUX, M. BOGEY, Y. LIU, M. CORDONNIER, *Laboratoire de Spectroscopie Hertzienne, Associé au C.N.R.S., U.F.R. de Physique, Université des Sciences et Technologies de Lille, Bât. P5, Villeneuve d'Ascq, 59655, France*; H. BÜRGER, M. SENZLOBER, *Anorganische Chemie, FB 9, Universität-Gesamthochschule, 42097, Wuppertal, Germany*; R. FAJGAR, J. POLA, *Institute of Chemical Process Fundamentals, Academy of Sciences, 16502, Prague 6, Czech Republic.*

WF10

15 min 4:17

DETERMINATION OF THE GEOMETRIC STRUCTURE OF BUTATRIENYLIDENE, H_2CCCC , AND OF THE HYPERFINE STRUCTURE OF PROPYNONYL, HCCCC

WEI CHEN, STEWART E. NOVICK, *Department of Chemistry, Wesleyan University, Middletown, CT 06459*; MICHAEL C. MCCARTHY, MICHAEL J. TRAVERS, P. THADDEUS, *Harvard-Smithsonian Center for Astrophysics, 60 Garden Street, and Division of Applied Sciences, Harvard University, 29 Oxford Street, Cambridge, MA 02138*; J. VRTILEK, *Harvard-Smithsonian Center for Astrophysics, 60 Garden Street, Cambridge, MA 02138*; C. A. GOTTLIEB, *Division of Applied Sciences, Harvard University, 29 Oxford Street, Cambridge MA 02138*; ANDREW L. COOKSY, *Department of Chemistry, University of Mississippi, University, MS 38677.*

WF11

15 min 4:34

MICROWAVE SPECTROSCOPY OF THE HCCS AND DCCS RADICALS IN THE VIBRONIC EXCITED STATES

JIAN TANG AND SHUJI SAITO, *Dept. of Molecular Structure, The Graduate University for Advanced Studies and Institute for Molecular Science, Okazaki 444, Japan.*

WF12

15 min 4:51

MILLIMETER-WAVE SPECTROSCOPY OF NCS:AN ANALYSIS OF VIBRONIC INTERACTION

TAKAYOSHI AMANO, *Institute for Astrophysics and Planetary Sciences, Ibaraki University, Mito 310, Japan.*

WF13

15 min 5:08

FOURIER-TRANSFORM MW SPECTROSCOPY OF THE $\text{SH}(\text{}^2\Pi_i)\text{-Ar}$ AND SD-Ar RADICAL COMPLEXES

YOSHIHIRO SUMIYOSHI, YASUKI ENDO, *Department of Pure and Applied Sciences, College of Arts and Sciences, The University of Tokyo, 153 Tokyo, Japan*; YASUHIRO OHSHIMA, *Department of Chemistry, Graduate School of Science, Kyoto University, 606-01 Kyoto, Japan*.

WF14

15 min 5:25

THE MICROWAVE SPECTRUM OF THE OPEN-SHELL COMPLEX NO-HF

C. R. DENNIS, C. J. WHITHAM, B. J. HOWARD, *The Physical and Theoretical Chemistry Laboratory South Parks Road, Oxford, OX1 3QZ, England*.

WF15

Post-deadline Abstract

15 min 5:42

LABORATORY SPECTROSCOPY OF THE C_7H AND C_8H RADICALS

MICHAEL C. McCARTHY, MICHAEL J. TRAVERS, AND P. THADDEUS, *Center for Astrophysics and Division of Applied Sciences, Harvard University, Cambridge, MA 02138*; CARL A. GOTTLIEB, *Division of Applied Sciences, Harvard University, Cambridge MA, 02138*.

WG. THEORY

WEDNESDAY, JUNE 12, 1996 – 1:30 PM

Room: 1005 SMITH LAB

Chair: PHILIP BUNKER, National Research Council of Canada, Ottawa, Canada

WG01 15 min 1:30

EXTRAPOLATION OF CARBON DIOXIDE LINE POSITIONS FOR HITEMP

ROBERT L. HAWKINS and LAURENCE S. ROTHMAN, *Simulation Branch, Geophysics Directorate, U.S. Air Force Phillips Laboratory, PL/GPOS, Hanscom AFB, MA 01731-3010.*

WG02 15 min 1:47

AN AB INITIO CALCULATION OF BH_2^- ROVIBRONIC ENERGIES: A VERY SMALL SINGLET-TRIPLET SPLITTING

J.-P. GU, G. HIRSCH, R. J. BUENKER, and PER JENSEN, *FB 9 - Theoretische Chemie, Bergische Universität - Gesamthochschule Wuppertal, D-42097 Wuppertal, Germany*; P. R. BUNKER, *Steacie Institute for Molecular Sciences, National Research Council of Canada, Ottawa, Ontario, Canada K1A 0R6.*

WG03 15 min 2:04

EXPERIMENTAL AND THEORETICAL STUDIES OF $\text{Mn}_2(\text{CO})_{10}$

HOLLY B. LAVENDER, TERRY GUSTAFSON, BRUCE BURSTEN, AND MARCELLO VITALE, *Department of Chemistry, The Ohio State University, Columbus, Ohio 43210.*

WG04 15 min 2:21

VIBRATIONAL PROPERTIES OF X_3^+ AND X_5^+ ($\text{X}=\text{F}, \text{Cl}, \text{Br}, \text{I}$) CLUSTERS IN MADELUNG POTENTIALS

JUN LI, *Department of Chemistry, The Ohio State University, Columbus, Ohio 43210*; W. H. E. SCHWARZ, *Theoretical Chemistry Laboratory, Department of Chemistry, University of Siegen, D-57068 Siegen, Germany.*

WG05 15 min 2:38

TUNNELING SPLITTINGS IN HYDROGEN-BONDED MOLECULES AND HYDROGEN TUNNELING IN CONDENSED PHASES

V. K. BABAMOV, *CAS, 2540 Olentangy River Road, Columbus, Ohio 43202, e-mail: vbabamov@cas.org.*

WG06 10 min 2:55

ANALYTICAL APPROXIMATION FOR ADIABATIC AND NONADIABATIC ELECTRONIC MATRIX ELEMENTS OF HOMONUCLEAR DIATOMIC RYDBERG STATES. APPLICATION TO SINGLET P-COMPLEX OF HYDROGEN MOLECULE

A.V. STOLYAROV AND V.I. PUPYSHEV, *Department of Chemistry, Moscow State University, Moscow 119899*; M.S. CHILD, *Theoretical Chemistry Department, Oxford University, Oxford OX1 3UB, UK.*

Intermission

WG07

15 min 3:20

AN EMPIRICAL MODEL FOR THE INFRARED COLLISION INDUCED ABSORPTION BAND OF N₂ NEAR 4.3 μ m

J. -M. HARTMANN, *LPMA, Université de Paris Sud (bât. 350), 91405 Orsay Cedex, France*;
W. J. LAFFERTY, *National Institute of Standards and Technology, Gaithersburg, MD 20899, USA*; A. M.
 SOLODOV, *Institute of Atmospheric Optics, Academy of Sciences, Akademicheskii Av. 1. Tomsk 634055,*
Russia; A. WEBER, *National Institute of Standards and Technology, Gaithersburg, MD 20899, USA*; W. B.
 OLSON, *348 N. Summit Ave., Gaithersburg, MD 20877, USA.*

WG08

15 min 3:37

VIBRATIONAL DEPENDENCE OF HYDROGEN-BROADENED HALFWIDTHS OF WATER VAPOR TRANSITIONS

R. GAMACHE, *Department of Environmental, Earth, and Atmospheric Sciences and Center for Atmospheric*
Research, University of Massachusetts, Lowell, MA 01854; R. LYNCH, *Wentworth Institute of Technology, 550*
Huntington Ave., Boston, MA 02135.

WG09

15 min 3:54

HALFWIDTHS AND LINE SHIFTS OF H₂O TRANSITIONS BROADENED BY CO₂

R. GAMACHE, *Department of Environmental, Earth, and Atmospheric Sciences and Center for Atmospheric*
Research, University of Massachusetts, Lowell, MA 01854; R. LYNCH, *Wentworth Institute of Technology, 550*
Huntington Ave., Boston, MA 02135.

WG10

15 min 4:11

ANALYSIS OF THE LINE POSITIONS AND LINE INTENSITIES IN THE ν_2 BAND OF THE WATER MOLECULE

L. H. COUDERT, *Laboratoire de Physique Moléculaire et Applications, C.N.R.S., Université Pierre et Marie*
Curie, Case Courrier 76, Tour 13, 4, Place Jussieu, F-75252 Paris Cedex 05, France.

WG11

10 min 4:28

MODELING OF THE FUNDAMENTAL RAMAN AND INFRARED CH STRETCHING SPECTRA OF CHD₂ PICOLINES

C. LAPOUGE, D. CAVAGNAT, *Laboratoire de Spectroscopie Moléculaire et Cristalline, URA 124, 351 crs de*
la Libération, 33405 Talence, FRANCE.

WG12

15 min 4:40

ON THE POSSIBILITY OF ESTIMATION HARMONIC FREQUENCIES OF MOLECULES (INTRAMOLECULAR FORCE FIELD PARAMETERS) ON THE BASE OF INFORMATION ABOUT ITS PURE ROTATIONAL SPECTRUM

O.N. ULENIKOV, S.N. YURTCHENKO, and R.N. TOLCHENOV, *Physics Department, Tomsk State Univer-*
sity, 634050, Tomsk, Russia.

WG13

15 min 4:57

CALCULATION OF THE SPECIFIC HEAT FROM THE RAMAN FREQUENCY DATA FOR NH₄Br

H. YURTSEVEN, *Department of Physics, Istanbul Technical University, Maslak, Istanbul, Turkey.*

WG14

15 min 5:14

PRECISE STUDY OF CHD_3 SPECTRUM IN THE REGION OF $1900\text{--}2800\text{ cm}^{-1}$

O.N. ULENIKOV and G.A. ONOPENKO, *Physics Department, Tomsk State University, 634050, Tomsk, Russia*; S. ALANKO, M. KOIVUSAARI, and R. ANTILA, *Department of Physics, University of Oulu, Linnanmaa, Oulu, Finland*.

WG15

Post-deadline Abstract

15 min 5:31

AB INITIO STUDY OF A QUASI VAN DER WAALS MOLECULE: N_2O_4 .

Y. ELYOUSSOUFI, J. LIEVIN and M. HERMAN, *Laboratoire de Chimie Physique Moléculaire, Université Libre de Bruxelles, CPI 160/09, B-1050 Bruxelles, BELGIUM*.

WG16

Post-deadline Abstract

10 min 5:48

LINE-MIXING EFFECTS IN Σ -II Q-BRANCHES OF CO_2 . TEMPERATURE, PRESSURE, AND PERTURBER DEPENDENCIES

R. RODRIGUES, *Laboratoire de Physique Moléculaire et Applications, Unité propre du CNRS (UPR 136) associé aux Universités Paris-Sud et P.&M. Curie, Université Paris-Sud (bât. 350), 91405 Orsay Cedex, France*; B. KHALIL, R. LE DOUCEN, *Département de Physique Atomique et Moléculaire, U.R.A. CNRS 1203, Université de Rennes I, Campus Beaulieu, 35042 Rennes Cedex, France*; J. M. HARTMANN, *Laboratoire de Physique Moléculaire et Applications, Unité propre du CNRS (UPR 136) associé aux Universités Paris-Sud et P.&M. Curie, Université Paris-Sud (bât. 350), 91405 Orsay Cedex, France*; and L. BONAMY, *Laboratoire de Physique Moléculaire, U.R.A. CNRS 772, Université de Franche-Comté, La Bouloie 25030 Besancon Cedex, France*.

WH. ELECTRONIC (SMALL)
WEDNESDAY, JUNE 12, 1996 – 1:30 PM
Room: 1008 EVANS LAB

Chair: MICHAEL MORSE, University of Utah, Salt Lake City, Utah

WH01**15 min 1:30**

ON THE LONG RANGE PART OF THE POTENTIAL CURVE OF THE $A^1\Sigma_u^+$ STATE IN ${}^6\text{Li}_2$

F. MARTIN, M. AUBERT-FRECON, R. BACIS, A. J. ROSS, P. CROZET, I. RUSSIER, S. MAGNIER, *Laboratoire de Spectrométrie Ionique et Moléculaire, UMR5579 CNRS et Université Lyon I, Bât 205 Campus La Loua, 69622 Villeurbanne Cedex, France*; C. LINTON, *Centre for Laser Applications and Molecular Science and Department of Physics, University of New Brunswick, PO Box 4400, Fredericton, NB, Canada, E3B 5A3.*

WH02**15 min 1:47**

ON THE $b^3\Pi_u$ STATE OF ${}^7\text{Li}_2$

I. RUSSIER, A. YIANNOPOULOU, A. J. ROSS, F. MARTIN, P. CROZET, R. BACIS, S. CHURASSY, *Laboratoire de Spectrométrie Ionique et Moléculaire, UMR5579 CNRS et Université Lyon I, Bât 205 Campus La Loua, 69622 Villeurbanne Cedex, France*; C. LINTON, *Centre for Laser Applications and Molecular Science and Department of Physics, University of New Brunswick, PO Box 4400, Fredericton, NB, Canada, E3B 5A3.*

WH03**15 min 2:04**

MULTIPLE RESONANCE SPECTROSCOPY OF THE $G^1\Pi_g$ AND $F^1\Sigma_g^+$ STATES OF ${}^7\text{Li}_2$: DETECTION OF PREDIS-SOCIATING $F^1\Sigma_g^+$ STATE LEVELS THROUGH ATOMIC SIDE FLUORESCENCE

S. ANTONOVA, K. URBANSKI, A. M. LYYRA, *Physics Department, Temple University, Philadelphia, PA 19122*; LI LI, *Department of Modern Applied Physics, Tsinghua University, Beijing.*

WH04**15 min 2:21**

COLLISIONAL TRANSFER AND GATEWAY EFFECT IN SINGLE AND DOUBLY EXCITED STATES OF Li_2

S. ANTONOVA, K. URBANSKI, A. M. LYYRA, *Physics Department, Temple University, Philadelphia, PA 19122*; LI LI, *Department of Modern Applied Physics, Tsinghua University, Beijing.*

WH05**15 min 2:38**

LOW-BARRIER ROTATION-PSEUDOROTATION HAMILTONIAN AND APPLICATION TO THE B STATE OF Na_3

NOBUKIMI OHASHI, MAKIKO TSUURA, *Department of Physics, Faculty of Science, Kanazawa University, Kakuma, Kanazawa, Japan 920-11*; JON T. HOUGEN, *Molecular Physics Division, National Institute of Standards and Technology, Gaithersburg, MD 20899*; WOLFGANG E. ERNST, *Department of Physics, The Pennsylvania State University, 104 Davey Laboratory, University Park, PA 16802*; STEFAN RAKOWSKY, *Max-Planck-Institut für Strömungsforschung, Bunsenstr. 10, D-37073 Göttingen, Germany.*

WH06**15 min 2:55**

OPTICAL-OPTICAL DOUBLE RESONANCE SPECTROSCOPY OF THE A-X AND B-X SYSTEMS OF Na_3

DAVID T. VITUCCIO, OLEG GOLONZKA, and WOLFGANG E. ERNST, *Department of Physics, The Pennsylvania State University, University Park, PA 16802.*

WH07

15 min 3:12

GLOBAL FIT OF THE B-X SYSTEM OF Na₃ USING A NEW MODEL HAMILTONIAN

OLEG GOLONZKA, DAVID T. VITUCCIO, and WOLFGANG E. ERNST, *Department of Physics, The Pennsylvania State University, University Park, PA 16802.*

Intermission

WH08

15 min 3:45

OPTICAL SINGLET AND TRIPLET BANDS OF HOMONUCLEAR ALKALI DIATOMICS ATTACHED TO COLD HELIUM CLUSTERS

J. HIGGINS, C. CALLEGARI, J. REHO, W. E. ERNST, and G. SCOLES, *Department of Chemistry, Princeton University, Princeton NJ 08544.*

WH09

15 min 4:02

OBSERVATION OF THE $2^3\Sigma_g^+-1^3\Sigma_u^+$ and $1^3\Pi_g-1^3\Sigma_u^+$ TRANSITIONS OF THE TRIPLET NaK MOLECULE ON THE SURFACE OF HELIUM CLUSTERS

J. HIGGINS, C. CALLEGARI, J. REHO, W. E. ERNST, K. K. LEHMANN, and G. SCOLES, *Department of Chemistry, Princeton University, Princeton, NJ 08544.*

WH10

15 min 4:19

DISPERSED FLUORESCENCE STUDIES OF QUARTET STATE ALKALI TRIMERS

J. HIGGINS, C. CALLEGARI, J. REHO, W. E. ERNST, K. K. LEHMANN, G. SCOLES, *Department of Chemistry, Princeton University, Princeton NJ 08544*; F. STIENKEMEIER, *Fakultät für Physik, Universität Bielefeld, Universitätsstr. 25, D-33615 Bielefeld, Germany*; M. GUTOWSKI, *Department of Chemistry, University of Gdansk, 80-952 Gdansk, Poland.*

WH11

15 min 4:36

VIBRATIONALLY RESOLVED NEGATIVE ION PHOTOELECTRON SPECTROSCOPIC STUDIES OF BARE TRANSITION METAL TRIMERS

S. ALEX, S. M. E. GREEN and D. G. LEOPOLD, *Department of Chemistry, University of Minnesota, Minneapolis MN 55455.*

WH12

15 min 4:53

VIBRATIONALLY RESOLVED NEGATIVE ION PHOTOELECTRON SPECTROSCOPIC STUDIES OF NIOBIUM CLUSTERS

S. M. E. GREEN, S. ALEX and D. G. LEOPOLD, *Department of Chemistry, University of Minnesota, Minneapolis, MN 55455.*

WH13

15 min 5:10

PRELIMINARY THEORETICAL AND EXPERIMENTAL STUDIES OF Al-GROUP14 DIATOMICS

BENOIT SIMARD, MARIE-ANGE LEBEAULT-DORGET, *Molecular Spectroscopy Group, Steacie Institute for Molecular Sciences, National Research Council of Canada, 100 Sussex Drive, Ottawa, Ontario, K1A 0R6.*

WH14**15 min 5:27**

FOURIER TRANSFORM EMISSION SPECTROSCOPY OF THE $B^1\Pi-X^1\Sigma^+$, $C^1\Sigma^+-X^1\Sigma^+$ AND $G^1\Pi-X^1\Sigma^+$ SYSTEMS OF ScH AND ScD

R. S. RAM, *Department of Chemistry, University of Arizona, Tucson, AZ 85721*; P. F. BERNATH, *Department of Chemistry, University of Waterloo, Waterloo, Ontario, Canada N2L 3G1*.

WH15**15 min 5:44**

FOURIER TRANSFORM EMISSION SPECTROSCOPY OF THE $g^4\Delta-a^4\Delta$ SYSTEM OF FeF

R. S. RAM, *Department of Chemistry University of Arizona, Tucson, AZ 85721*; P. F. BERNATH, *Department of Chemistry, University of Waterloo, Waterloo, Ontario, Canada N2L 3G1*; S. P. DAVIS, *Department of Physics, University of California, Berkeley, CA 94720*.

RA. SYMPOSIUM: COHERENT IR

THURSDAY, JUNE 13, 1996 – 8:30 AM

Room: 1153 SMITH LAB

Chair: ARLAN MANTZ, Connecticut College, New London, Connecticut
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RA01

INVITED TALK

30 min 8:30

LASER FREQUENCY SPECTROSCOPY: A REVIEW

K. M. EVENSON, *Time and Frequency Division, National Institute of Standards and Technology, Boulder, CO 80303.*

RA02

15 min 9:05

THEORY AND EXPERIMENTAL CHARACTERIZATION OF LEAD SALT DIODE LASER FREQUENCY MODULATION SPECTROSCOPY

KHOSROW NAMJOU, CHI KONG NG, EDWARD A. WHITTAKER, *Department of Physics and Engineering Physics, Stevens Institute of Technology, Hoboken, NJ 07030.*

RA03

15 min 9:22

HIGH PRECISION TUNABLE DIODE LASER CONTROL: APPLICATION TO THE STUDY OF DICKE NARROWING

A. HENRY, D. HURTMANS, M. MARGOTTIN-MACLOU and A. VALENTIN, *Laboratoire de Physique Moléculaire et Applications, C.N.R.S., Université Pierre et Marie Curie, Boîte 76, Tour 13, 4, Place Jussieu, F-75252 Paris Cedex 05, France.*

RA04

15 min 9:39

SUB-DOPPLER SATURATION SPECTROSCOPY WITH THE COLOGNE THZ SPECTROMETER

S.P. BELOV, G. WINNEWISSER and TH. KLAUS, *I. Physikalisches Institut, Universität zu Köln, Zöllicher Str. 77, D-50937 Cologne, Germany.*

RA05

15 min 9:56

PRESSURE BROADENING AND SHIFT OF SOME NH₃ LINES MEASURED BY DIODE LASER SPECTROSCOPY

KOICHI M. T. YAMADA, M. FABIAN, *National Institute for Advanced Interdisciplinary Research, Tsukuba 305, Japan*; R. SCHIEDER, and G. WINNEWISSER, *I. Physikalisches Institut, Universität zu Köln, D-50937 Köln, Germany.*

RA06

15 min 10:13

THE VARIABLE TEMPERATURE PRESSURE BROADENING AND LINE SHIFT OF CO AND HDO IN COLLISION WITH HELIUM

M. M. BEAKY, T. M. GOYETTE, and F. C. DE LUCIA, *Department of Physics, The Ohio State University, 174 West 18th Avenue, Columbus OH 43210-1106.*

RA07

10 min 10:30

PRELIMINARY RESULTS FROM METHYL CHLORIDE COLLISIONAL COOLING EXPERIMENTS

A. W. MANTZ, *Department of Physics and Astronomy, Connecticut College, 270 Mohegan Ave., New London, CT 06320-4196*; C. BALL, and F. C. DE LUCIA, *Department of Physics, The Ohio State University, Columbus, Ohio 43210*.

Intermission

RA08

15 min 11:00

HIGH-RESOLUTION $\nu_{OH}=3\leftarrow 0$ OVERTONE SPECTROSCOPY OF HOD

JOANNA R. FAIR, ONDREJ VOTAVA, and DAVID J. NESBITT, *JILA, National Institute of Standards and Technology and Department of Chemistry and Biochemistry, University of Colorado, Boulder, CO 80309-0440*.

RA09

10 min 11:17

LASER SPECTROSCOPY OF 3ν , 5ν AND 6ν VIBRATION - ROTATION BANDS OF HBr

N. NISHIMIYA, T. YUKIYA AND M. SUZUKI, *Dept. of Electronic Engineering, Tokyo Institute of Polytechnics, Iiyama 1583, Atsugi City, 243-02 Kanagawa, Japan*.

RA10

15 min 11:29

VIBRATIONAL-ROTATIONAL-TUNNELING SPECTROSCOPY OF N_2 - D_2O WITH AN ALL SOLID STATE, OPTICAL HETERODYNE, SUBMILLIMETER-WAVE SPECTROMETER

PIN CHEN, *Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, CA 91125*; GEOFFREY A. BLAKE, *Division of Geological and Planetary Sciences, California Institute of Technology, Pasadena, CA 91125*.

RA11

15 min 11:46

LASER SIDE BAND SPECTRUM OF THE ν_2/ν_4 DIAD OF AsH_3 AND PH_3 ; SATURATION OF PERTURBATION ALLOWED TRANSITIONS

G. SPIEGL, A. AINETSCHIAN, and W. A. KREINER, *Department of Chemistry, University of Ulm, D-89069 ULM, Germany*.

RA12

15 min 12:03

FAR-INFRARED LASER STARK SPECTROSCOPY OF PH_3

M. JACKSON, *Department of Physics, New Mexico State University, Las Cruces, NM 88003*; G. R. SUDHAKARAN and E. GANSEN, *Department of Physics, University of Wisconsin, La Crosse, WI 54601*.

RB. ELECTRONIC (LARGE)
THURSDAY, JUNE 13, 1996 – 8:30 AM

Room: 1009 SMITH LAB

Chair: MASARU FUKUSHIMA, Mitsubishi Heavy Industries, Yokohama, Japan
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RB01 **15 min 8:30**
 REMPI SPECTRA AND AB INITIO CALCULATIONS OF BENZOTRIAZOLE AND ITS WATER CLUSTERS

MICHAEL SCHMITT, WOLFGANG ROTH, CHRISTOPH JACOBY and KARL KLEINERMANN, *Institut für Physikalische Chemie und Elektrochemie I, Heinrich-Heine Universität Düsseldorf, Germany.*

RB02 **15 min 8:47**
 FLUORESCENCE DIP INFRARED SPECTROSCOPY (FDIRS) OF JET-COOLED 5-HYDROXYTROPOLONE

R. K. FROST AND T. S. ZWIER, *Department of Chemistry, Purdue University, West Lafayette, IN 47907-1393.*

RB03 **15 min 9:04**
 INFRARED SPECTROSCOPY OF JET-COOLED TROPOLONE AND TROPOLONE-OD IN THE O-H AND C-H STRETCH REGION

C. A. ARRINGTON, R. K. FROST, F. C. HAGEMEISTER, AND T. S. ZWIER, *Department of Chemistry, Purdue University, West Lafayette, IN 47907-1393.*

RB04 **15 min 9:21**
 FLUORESCENCE-DIP INFRARED SPECTROSCOPY OF THE TROPOLONE-H₂O COMPLEX

F. C. HAGEMEISTER, C. A. ARRINGTON, R. K. FROST, D. SCHLEPPENBACH, AND T. S. ZWIER, *Department of Chemistry, Purdue University, West Lafayette, IN 47907-1393*; K. D. JORDAN, *Department of Chemistry, University of Pittsburgh, Pittsburgh, PA 15260.*

RB05 **15 min 9:38**
 TIME RESOLVED STIMULATED EMISSION PUMPING OF BIANTHRYL-WATER COMPLEXES

BRIAN A. PRYOR, PETER M. ANDREWS, and MICHAEL R. TOPP, *Department of Chemistry, University of Pennsylvania, Philadelphia, Pennsylvania 19104.*

RB06 **15 min 9:55**
 DOUBLE RESONANCE STUDY OF HYDROGEN-BONDED PERYLENE COMPLEXES

PETER M. ANDREWS, BRIAN A. PRYOR, and MICHAEL R. TOPP, *Department of Chemistry, University of Pennsylvania, Philadelphia, PA 19104 andrews@chem.upenn.edu.*

Intermission

RB07**10 min 10:30****VIBRATIONAL OVERTONE SPECTROSCOPY OF ORGANOMETALLIC COMPLEXES**

A. V. FEDEROV and D. SNAVELY, *Center for Photochemical Sciences, Department of Chemistry, Bowling Green State University, Bowling Green OH 43403.*

RB08**15 min 10:42****STRUCTURE AND DYNAMICS OF ANILINE-Ar FROM HIGH RESOLUTION ELECTRONIC SPECTROSCOPY IN THE GAS PHASE**

WAYNE E. SINCLAIR and DAVID W. PRATT, *Department of Chemistry, University of Pittsburgh, Pittsburgh, PA 15260.*

RB09**15 min 10:59****STRUCTURES AND VIBRATIONS OF PHENOL-NH₃ AND PHENOL-(NH₃)₃-CLUSTERS**

C. JACOBY, C. DEUSEN, A. SCHIEFKE, M. GERHARDS, K. KLEINERMANNS, *Heinrich-Heine-Universität Düsseldorf, Institut für Physikalische Chemie und Elektrochemie I, Universitätsstraße 26.43.02, 40225 Düsseldorf;* and P. HERING, *Heinrich-Heine-Universität Düsseldorf, Institut für Lasermedizin, Universitätsstraße 26.43.02, 40225 Düsseldorf.*

RB10**15 min 11:16****THE T₁(Nπ*)←S₀ LASER INDUCED PHOSPHORESCENCE EXCITATION SPECTRUM OF ACETALDEHYDE IN A SUPERSONIC FREE JET: TORSION AND WAGGING POTENTIALS IN THE LOWEST TRIPLET STATE**

H. LIU, E. C. LIM, *Department of Chemistry, The University of Akron, Akron, OH 44325-3601;* C. MUÑOZ-CARO, A. NINO, *E. U. Informática, Universidad de Castilla-La Mancha, Ronda de Calatrave 5, 13071 Ciudad Real, Spain;* R. H. JUDGE, *Department of Chemistry, University of Wisconsin-Parkside, Kenosha, WI 53141-2000;* D. C. MOULE, *Department of Chemistry, Brock University, St. Catharines, Ontario, L2S 3A1, Canada.*

RB11**15 min 11:33****ELECTRONIC SPECTROSCOPY OF DIPHENYLAMINE AND ITS SOLVENT CLUSTERS**

IGOR V. TRETIKOV and JOHN R. CABLE, *Department of Chemistry and Center for Photochemical Sciences, Bowling Green State University, Bowling Green, OH 43403.*

RB12*Post-deadline Abstract***15 min 11:50****AB INITIO STUDY OF THE np (n=3-5) AND 4s-3d RYDBERG COMPLEXES OF ACETYLENE**

F. LARUELLE and J. LIEVIN, *Laboratoire de Chimie Physique Moléculaire, Université Libre de Bruxelles, CPI 160/09, B-1050 Bruxelles, BELGIUM.*

RC. RADICALS

THURSDAY, JUNE 13, 1996 – 8:30 AM

Room: 1005 SMITH LAB

Chair: TREVOR SEARS, Brookhaven National Laboratory, Upton, New York

RC01 15 min 8:30

OPTICAL STARK SPECTROSCOPY OF CaCH_3

A. J. MARR and T. C. STEIMLE, *Dept. of Chemistry and Biochemistry, Arizona State University, Tempe, AZ 85287-1604.*

RC02 10 min 8:47

HIGH RESOLUTION LASER SPECTROSCOPY OF THE $\tilde{C}^2A_1-\tilde{X}^2A_1$ TRANSITION OF CaNH_2

ZULFIKAR MORBI, CHUNFENG ZHAO, and P. F. BERNATH, *Center for Molecular Beams and Laser Chemistry, University of Waterloo, Waterloo, Ont., Canada, N2L 3G1.*

RC03 10 min 8:59

HIGH RESOLUTION LASER SPECTROSCOPY OF THE $\tilde{C}^2A_1-\tilde{X}^2A_1$ TRANSITION OF SrNH_2 AND $\tilde{B}^2B_1-\tilde{X}^2A_1$ TRANSITION OF CaNH_2

CHUNFENG ZHAO, J. W. HEPBURN, P. F. BERNATH, *Center for Molecular Beams and Laser Chemistry, University of Waterloo, Waterloo, Ont. Canada, N2L 3G1.*

RC04 15 min 9:11

LASER SPECTROSCOPY OF CCH IN THE $36600\text{--}29700\text{ cm}^{-1}$ REGION

WHE-YI CHIANG and YEN-CHU HSU, *Institute of Atomic and Molecular Sciences, Academia Sinica, P. O. Box 23-166, Taipei 107, Taiwan, Republic of China and Department of Chemistry, National Taiwan University, Taipei 107, Republic of China.*

RC05 15 min 9:28

FLUORESCENCE LIFETIMES OF THE \tilde{B}^2A' STATE OF CCH

WHE-YI CHIANG and YEN-CHU HSU, *Institute of Atomic and Molecular Sciences, Academia Sinica, P. O. Box 23-166, Taipei 107, Taiwan, Republic of China and Department of Chemistry, National Taiwan University, Taipei 107, Taiwan, R.O.C..*

RC06 15 min 9:45

PULSED DISCHARGE JET SPECTROSCOPY OF THE $\tilde{A}^1A''-\tilde{X}^1A'$ BAND SYSTEMS OF SILYLENES AND GERMYLENES

WARREN W. HARPER, H. HARJANTO, and DENNIS J. CLOUTHIER, *Department of Chemistry, University of Kentucky, Lexington, KY 40506-0055.*

Intermission

RC07 *Original abstract withdrawn—replaced with post-deadline abstract* 15 min 10:20

REMPI SPECTROSCOPY OF THE $3p\pi^2\Pi$ RYDBERG STATE OF HCO

HARTMUT G. HEDDERICH, ERIC E. MAYER, and EDWARD R. GRANT, *Department of Chemistry, Purdue University, West Lafayette, IN 47907-1393.*

RC08 15 min 10:37

THE VIBRATIONAL/ROTATIONAL ASSIGNMENT OF THE LIF SPECTRUM OF THE \tilde{A}^2A_1 - \tilde{X}^2E ELECTRONIC TRANSITION OF THE METHOXY RADICAL

MICHAEL B. PUSHKARSKY, DAVID E. POWERS, and TERRY A. MILLER, *The Ohio State University, Department of Chemistry, The Laser Spectroscopy Facility, 120 West 18th Ave., Columbus, OH 43210.*

RC09 15 min 10:54

FLUORESCENCE DEPLETION SPECTROSCOPY FOR MAPPING DARK VIBRONIC LEVELS IN THE \tilde{A}^2A_1 STATE OF THE METHOXY RADICAL

DAVID E. POWERS, MICHAEL B. PUSHKARSKY, and TERRY A. MILLER, *The Ohio State University, Department of Chemistry, The Laser Spectroscopy Facility, 120 West 18th Ave., Columbus, OH 43210.*

RC10 15 min 11:11

ROTATIONAL ANALYSIS OF A-E AND E-E VIBRONIC BANDS OF CF₃S

MIN-CHIEH YANG, DAVID E. POWERS, CHRISTOPHER C. CARTER, JAMES M. WILLIAMSON, and TERRY A. MILLER, *The Ohio State University, Department of Chemistry, The Laser Spectroscopy Facility, 120 West 18th Ave., Columbus, OH 43210.*

RC11 10 min 11:28

JAHN-TELLER AND SPIN-ORBIT COUPLING IN THE 2E GROUND STATE OF CF₃O AND CF₃S

TIMOTHY A. BARCKHOLTZ AND TERRY A. MILLER, *Laser Spectroscopy Facility, Department of Chemistry, The Ohio State University, Columbus, Ohio 43210.*

RC12 15 min 11:40

VIBRONIC ANALYSIS OF THE $B\ ^2A' - X\ ^2A''$ LASER-INDUCED FLUORESCENCE OF JET-COOLED ETHYLTHIO (C₂H₅S)

YUAN-PERN LEE, MIN-YI SHEN, and WEN-CHING HUNG, *Department of Chemistry, National Tsing Hua University, Hsinchu, TAIWAN 30043.*

RC13 15 min 11:57

LASER INDUCED FLUORESCENCE SPECTROSCOPY OF THE C₄H AND C₄D RADICALS

K. HOSHINA, H. KOHGUCHI, AND Y. ENDO, *Department of Pure and Applied Sciences, College of Arts and Sciences, The University of Tokyo, 153 Tokyo, Japan*; Y. OHSHIMA, *Department of Chemistry, Graduate School of Science, Kyoto University, 606-01 Kyoto, Japan.*

RD. THEORY

THURSDAY, JUNE 13, 1996 – 8:30 AM

Room: 1008 EVANS LAB

Chair: RUSSELL PITZER, The Ohio State University, Columbus, Ohio

RD01 **INVITED TALK** **30 min 8:30**

AB INITIO STUDY OF PHOTODISSOCIATION OF SEVERAL SMALL MOLECULES

K. MOROKUMA and Q. CUI, *Cherry L. Emerson Center for Scientific Computation and Department of Chemistry, Emory University, Atlanta, GA, 30322.*

RD02 **15 min 9:05**

EXCITATION OF COUPLED ELECTRONIC STATES

S. T. GIBSON, and B. R. LEWIS, *Research School of Physical Sciences and Engineering, The Australian National University, Canberra ACT 0200, Australia (email: Stephen.Gibson@anu.edu.au); P. C. COSBY, Molecular Physics Laboratory, SRI International, Menlo Park CA 94025.*

RD03 **15 min 9:22**

AB INITIO CALCULATION OF BiN SPECTRUM: CAN $^5\Sigma^+ - ^1\Sigma$ TRANSITIONS BE OBSERVED?

ALEKSEY B. ALEKSEYEV, H.-P. LIEBERMANN, G. HIRSCH AND R.J. BUENKER, *Theoretische Chemie, Bergische Universität, D-42097 Wuppertal, Germany.*

RD04 **10 min 9:39**

THE ELECTRONIC STRUCTURE OF LiAl AND ITS POSITIVE ION

DANIEL B. LAWSON and JAMES F. HARRISON, *Department of Chemistry, Michigan State University, East Lansing, MI 48824-1322.*

RD05 **10 min 9:51**

AB-INITIO STUDY OF SEVERAL LOW-LYING STATES OF YN

JESSE EDWARDS and JAMES F. HARRISON, *Department of Chemistry, Michigan State University, East Lansing, MI 48824-1322.*

RD06 **10 min 10:03**

GROUND-STATE SPLITTING OF Am^{2+} IN CaF_2

SCOTT R. BROZELL AND RUSSELL M. PITZER, *Department of Chemical Physics, The Ohio State University, Columbus, OH 43210.*

Intermission

RD07**15 min 10:30**JAHN-TELLER EFFECT IN VCl_4

KE ZHAO and RUSSELL M. PITZER, *Department of Chemistry, The Ohio State University, Columbus, OH 43210.*

RD08**15 min 10:47**AB INITIO CALCULATION OF $\text{U}(\text{BH}_4)_4$

ZHIYONG ZHANG and RUSSELL M. PITZER, *Department of Chemical Physics, The Ohio State University, Columbus, OH 43210.*

RD09**15 min 11:04**

VARIATIONAL QUANTUM MONTE CARLO CALCULATIONS INCLUDING SPIN-ORBIT COUPLING

HEINZ-JÜRGEN FLAD, MICHAEL DOLG and ALOK SHUKLA, *Max-Planck-Institut für Physik komplexer Systeme (Aussenstelle Stuttgart), D-70569 Stuttgart, Germany.*

RD10**15 min 11:21**

MOLECULAR MULTICENTER INTEGRALS OF SPHERICAL GAUSSIAN FUNCTIONS BY GENERALIZED GRADIENT OPERATOR METHOD

L. -Y. CHOW CHIU, *Department of Chemistry, Howard University, Washington DC 20059;*
M. MOHARERRZADEH, *Natural Sciences and Mathematics Department, Bowie State University, Bowie, MD 20715.*

RD11**15 min 11:38**THE VIBRATIONAL FREQUENCIES OF HALOSILYLENES HSiX ($\text{X}=\text{F}, \text{Cl}, \text{Br}$)

KALVIN J. GREGORY and ROGER S. GREV, *Department of Chemistry, The University of Kentucky, Lexington KY 40506.*

RD12**15 min 11:55**AB INITIO STUDIES OF THE Ar-NO^+ CATIONIC COMPLEX USING HIGH LEVEL CALCULATIONS

A. M. BUSH, T. G. WRIGHT, *Chemistry Department, The University, Highfield, Southampton, SO17 1BJ United Kingdom;* V. SPIRKO, *J. Heyrovský Institute of Physical Chemistry, Academy of Sciences of the Czech Republic, 18223 Prague 8, Dolejskova 3, Czech Republic.*

RE. ELECTRONIC (SMALL)
THURSDAY, JUNE 13, 1996 – 1:30 PM

Room: 1153 SMITH LAB

Chair: WOLFGANG ERNST, Pennsylvania State University, University Park, Pennsylvania
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RE01 **15 min 1:30**

NEAR-DISSOCIATION THEORY ANALYSIS FOR THE DISSOCIATION ENERGY AND VIBRATIONAL EXTRAPOLATION FOR $\text{Ba}^+ - \text{Ar}$

ROBERT J. LE ROY, *Guelph-Waterloo Centre for Graduate Work in Chemistry, University of Waterloo, Waterloo, Ontario N2L 3G1, Canada.*

RE02 **15 min 1:47**

MICROWAVE SPECTROSCOPY OF THE LONG-RANGE $\text{Ne} \cdots \text{Ne}^+ (^2\text{P})$ ION

ALAN CARRINGTON, DAVID I. GAMMIE, ANDREW M. SHAW and SUSIE M. TAYLOR, *Department of Chemistry, University of Southampton, Southampton SO17 1BJ, UK.*

RE03 **15 min 2:04**

PHOTODISSOCIATION SPECTROSCOPY OF Ca^+ -RARE GAS COMPLEXES

S. H. PULLINS, C. T. SCURLOCK, J. E. REDDIC, and M. A. DUNCAN, *Department of Chemistry, University of Georgia, Athens, GA 30602.*

RE04 **15 min 2:21**

PHOTOIONIZATION SPECTROSCOPY OF IONIC METAL DIMERS: CuLi AND AgLi

L. R. BROCK, A. M. KNIGHT, J. E. REDDIC, J. S. PILGRIM and M. A. DUNCAN, *Department of Chemistry, University of Georgia, Athens, GA 30602.*

RE05 **15 min 2:38**

THE (1+1) REMPI SPECTROSCOPY OF $\text{Rg} \cdot \text{NO}$ ($\text{Rg} = \text{Ar}, \text{Kr}$) VIA THE $\tilde{\text{A}}^2\Sigma^+$ ELECTRONIC STATE

A. M. BUSH, J. M. DYKE, P. MACK, D. M. SMITH, and T. G. WRIGHT, *Chemistry Department, The University, Highfield, Southampton, SO17 1BJ United Kingdom.*

RE06 **15 min 2:55**

EXPLANATION OF WHY THE RESONANT STRUCTURE SEEN IN THE (1+1) REMPI SPECTRUM OF $\text{Kr} \cdot \text{NO}$ VIA THE $\tilde{\text{A}}^2\Sigma^+$ STATE APPEARS IN THE Kr^+ MASS CHANNEL AS WELL AS THE $\text{Kr} \cdot \text{NO}^+$ MASS CHANNEL

A. M. BUSH, J. M. DYKE, P. MACK, D. M. SMITH, and T. G. WRIGHT, *Chemistry Department, The University, Highfield, Southampton, SO17 1BJ United Kingdom.*

RE07

15 min 3:12

O₂ PHOTOABSORPTION IN THE 40950-41300 CM⁻¹ REGION: NEW HERZBERG BANDS, NEW ABSORPTION LINES, AND IMPROVED SPECTROSCOPIC DATA

T. G. SLANGER, D. L. HUESTIS, and P. C. COSBY, *Molecular Physics Laboratory, SRI International, Menlo Park, CA 94025*; H. NAUS and G. MEIJER, *Dept. of Molecular and Laser Physics, University of Nijmegen, Toernooiveld 1, 6525 ED Nijmegen, The Netherlands*.

Intermission

RE08

10 min 3:45

LASER INDUCED FLUORESCENCE STUDY OF THE EFFECT OF PERTURBATIONS ON THE RADIATIVE LIFETIMES AND COLLISIONAL RELAXATION OF THE CO(a' ³Σ⁺, v'=31 AND 35) STATES

G. ZIKRATOV, D. W. SETSER, *Department of Chemistry, Kansas State University, Manhattan, KS 66502*; N. SADEGHI, *Laboratoire de Spectrometrie Physique, Universite Joseph Fourier-Grenoble I, B. P. 87, 38402 St. Martin d'Heres, France*.

RE09

15 min 3:57

THE EMISSION CONTINUUM OF ELECTRON EXCITED MOLECULAR HYDROGEN

X. LIU, *Jet Propulsion Laboratory, Pasadena, CA 91109*; D. E. SHEMANSKY, *University of Southern California, Los Angeles, CA 90089*; H. ABGRALL, and E. ROUEFF, *Observatoire de Paris, Section de Meudon, 92195 Meudon Cedex, France*.

RE10

15 min 4:14

HIGH-RESOLUTION SPECTROSCOPY USING A CCD ARRAY DETECTOR: THE A → X SYSTEM IN OH

J. TELLINGHUISEN, *Department of Chemistry, Vanderbilt University, Nashville, TN 37235*.

RE11

15 min 4:31

A STUDY OF CORE NON-PENETRATING RYDBERG STATES OF CaF

H. MA, *Department of Physics, Tsinghua University, Beijing 100084, China*; Y. M. LIU, J. LI, W. F. POLIK, K. L. CUNNINGHAM, and R. W. FIELD, *Department of Chemistry, MIT, 77 Mass. Ave., Cambridge, MA 02139*.

RE12

10 min 4:48

ON THE LEAST-SQUARES FITTING OF CORRELATED DATA: A PRIORI VS A POSTERIORI WEIGHTING

J. TELLINGHUISEN, *Department of Chemistry, Vanderbilt University, Nashville, TN 37235*.

RE13

15 min 5:00

THE B(1/2²P_{3/2}) → X(1/2²Σ⁺) TRANSITION IN XeBr

JASON O. CLEVINGER, *Department of Chemistry, MIT, Cambridge, MA 02139*; and JOEL TELLINGHUISEN, *Department of Chemistry, Vanderbilt University, Nashville, Tennessee 37235*.

RE14**15 min 5:17**THE $B \rightarrow X$ TRANSITION IN XeI

D. RADZYKEWYCZ and J. TELLINGHUISEN, *Department of Chemistry, Vanderbilt University, Nashville, TN 37235.*

RE15**10 min 5:34**LASER SPECTROSCOPY OF THE $A^3\Pi_{1u} \leftarrow X^1\Sigma_g^+$ SYSTEM OF I_2 IN THE 11650–12300 CM^{-1} REGION

TOKIO YUKIYA, NOBUO NISHIMIYA and MASAO SUZUKI, *Department of Electronic Engineering, Tokyo Institute of Polytechnics, Iiyama 1583, Atsugi City, 243-02 Kanagawa, Japan.*

RE16**10 min 5:46**

OBSERVATION OF LUMINESCENCE SPECTRA OF KrD RYDBERG MOLECULE AT LOW (40K) TEMPERATURE

A. A. PELMENEV, E. B. GORDON, V. V. KHMELLENKO, M. V. MARTYNENKO, E. A. POPOV, *Institute for Energy Problems of Chemical Physics, 142432, Chernogolovka, Moscow Region, Russia.*

RF. MATRIX AND CONDENSED PHASE

THURSDAY, JUNE 13, 1996 – 1:30 PM

Room: 1009 SMITH LAB

Chair: JULANNA GILBERT, University of Denver, Denver, Colorado

RF01 15 min 1:30

ANALYSIS OF THE Q_1 (1) IMPURITY NEXT NEAREST NEIGHBOR (NNN) PAIR SPECTRUM IN SOLID PARAHYDROGEN AND NON-RESONANT VIBRON HOPPING

YU ZHANG, TERESA J. BYERS, DAVID P. WELIKY, and TAKESHI OKA, *Department of Chemistry, Department of Astronomy and Astrophysics, and Department of Physics, The University of Chicago, Chicago, IL 60637-1403.*

RF02 10 min 1:47

NEW INFRARED TRANSITIONS OF SOLID PARAHYDROGEN IN THE SPECTRAL REGION 7900 - 9900 CM^{-1}

M. MENGEL, B. P. WINNEWISSER and M. WINNEWISSER, *Physikalisch-Chemisches Institut, Justus-Liebig-Universität, Heinrich-Buff-Ring 58, D-35392 Giessen.*

RF03 15 min 1:59

EXTENDED OBSERVATION AND ANALYSIS OF THE FIRST OVERTONE SPECTRUM OF SOLID PARAHYDROGEN

M. MENGEL, B. P. WINNEWISSER AND M. WINNEWISSER, *Physikalisch-Chemisches Institut, Justus-Liebig-Universität, Heinrich-Buff-Ring 58, D-35392 Giessen.*

RF04 15 min 2:16

INFRARED SPECTROSCOPIC STUDY OF CARBON CLUSTERS TRAPPED IN SOLID PARAHYDROGEN

TAKAMASA MOMOSE, MASAOKI MIKI, TOMONARI WAKABAYASHI, AND TADAMASA SHIDA, *Division of Chemistry, Graduate School of Science, Kyoto University, Kyoto 606-01, JAPAN.*

RF05 15 min 2:33

LASER INDUCED FLUORESCENCE AND BEAM DEPLETION SPECTROSCOPY OF K ATOMS ATTACHED TO LARGE HYDROGEN CLUSTERS

C. CALLEGARI, F. STIENKEMEIER ^a, J. HIGGINS, and G. SCOLES, *Department of Chemistry, Princeton University, Princeton, New Jersey 08544.*

^aPresent address: Fakultät für Physik, Universität Bielefeld, D-33615 Bielefeld, Germany

RF06 15 min 2:50

TRANSITION-METAL MONOSILONYLS [$\text{M}(\text{SiO})$, $\text{M}=\text{Cu}, \text{Ag}, \text{Au}, \text{V}$]: ESR AT 4 K

A. P. WILLIAMS, R. J. VAN ZEE, and W. WELTNER, JR., *Department of Chemistry, University of Florida, Gainesville, FL 32611.*

RF07

15 min 3:07

COOPERATIVE EFFECTS IN OPTICAL AND ESR SPECTROSCOPY OF NITROGEN ATOMS ISOLATED BY SOLIDIFIED HELIUM

E. B. GORDON, R. E. BOLTNEV, V. V. KHMELLENKO, M. V. MARTYNENKO, A. A. PELMENEV, and E. A. POPOV, *Institute for Energy Problems of Chemical Physics (branch), 142432 Chernogolovka, Moscow Region, Russian Federation.*

Intermission

RF08

15 min 3:40

ABSOLUTE INFRARED ABSORPTION INTENSITIES OF LIQUID MIXTURES OF CH₃CN AND H₂O

JOHN E. BERTIE and ZHIDA LAN, *Department of Chemistry, University of Alberta, Edmonton, Alberta, T6G 2G2 Canada.*

RF09

15 min 3:57

THE FTIR STUDY OF THE UV IRRADIATION OF AMORPHOUS AND CRYSTALLINE ACETYL CHLORIDE

BRAD ROWLAND and WAYNE HESS, *Battelle Pacific Northwest Laboratories, PO Box 999, Richland, WA. 99352, Mail Stop K2-14.*

RF10

15 min 4:14

THE INTERACTION OF STRONG HYDROGEN-BONDING MOLECULES WITH THE SURFACE OF NANO-SIZED CRYSTALLINE ICE CLUSTERS

LANCE DELZEIT and J. PAUL DEVLIN, *Department of Chemistry, Oklahoma State University, Stillwater, OK 74078.*

RF11

15 min 4:31

COMPARATIVE STUDIES OF THE TRIPLET MONOCYCLIC AROMATIC DIAZINES UNDER PRESSURE

I. Y. CHAN, W. WANG, *Department of Chemistry, Brandeis University, Waltham MA 02254.*

RF12

15 min 4:48

THE EFFECT OF EXTERNAL PRESSURE ON THE HIGH SPIN TO LOW SPIN TUNNELING RATE OF A Fe(II) SPIN CROSSOVER SYSTEM

W. WANG, I. Y. CHAN, *Department of Chemistry, Brandeis University, Waltham MA 02254.*

RF13

15 min 5:05

HIGH PRESSURE STUDIES OF J-AGGREGATES

I. Y. CHAN, *Department of Chemistry, Brandeis University, Waltham MA 02254*; M. LINDRUM, *Fachbereich Physik, Free University, Berlin, Germany.*

RF14**15 min 5:22****PENETRATION DEPTHS OF PHOTOMOBILIZED F ATOMS FROM A SANDWICH EXPERIMENT**

C. BRESSLER, M. DICKGIESSER, and N. SCHWENTNER, *Institut für Experimentalphysik, Freie Universität Berlin, Arnimallee 14, D-14195 Berlin, Germany.*

RF15**15 min 5:39****INFRARED SPECTROSCOPY AND PHOTOCHEMISTRY OF NITROMETHANE ADSORBED ON ALKALI HALIDE FILMS**

MARGARET CULLEN, GERALD WAYTON, and C. A. BAUMANN, *Department of Chemistry, University of Scranton, Scranton, PA 18510.*

RG. MICROWAVE

THURSDAY, JUNE 13, 1996 – 1:30 PM

Room: 1005 SMITH LAB

Chair: MICHAEL TUBERGEN, Kent State University, Kent, Ohio
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RG01

10 min 1:30

PRESSURE BROADENING OF AMMONIA INVERSION STATES FROM 5-30 K

D. R. WILLEY, P. DENARDO, T. TYSZKA, and R. TIMLIN, *Department of Physics, Allegheny College, Meadville, PA 16335.*

RG02

15 min 1:42

VARIABLE TEMPERATURE PRESSURE BROADENING OF H₂S

C. D. BALL, *Department of Physics, The Ohio State University, 174 West 18th Avenue, Columbus, OH 43210-1106*; J. M. DUTTA, *Department of Physics, North Carolina Central University, Durham NC 27707*; T. M. GOYETTE, *Department of Physics, The Ohio State University, 174 West 18th Avenue, Columbus, OH 43210-1106*; P. HELMINGER, *Department of Physics, University of South Alabama, Mobile, AL 36688*; F. C. DE LUCIA, *Department of Physics, The Ohio State University, 174 West 18th Avenue, Columbus, OH 43210-1106.*

RG03

10 min 1:59

THE VARIABLE TEMPERATURE PRESSURE BROADENING OF H₂S IN COLLISION WITH HYDROGEN

D. C. FLATIN, C. BALL, and F. C. DE LUCIA, *Department of Physics, The Ohio State University 174 West 18th Avenue, Columbus, OH 43210-1106.*

RG04

15 min 2:11

FURTHER INVESTIGATIONS OF THE BrO ROTATIONAL SPECTRUM

EDWARD A. COHEN and HOLGER S. P. MÜLLER, *Jet Propulsion Laboratory, California Institute of Technology, Pasadena, California 91109.*

RG05

15 min 2:28

THE ν_1 and ν_2 BANDS OF DOBr AND THE ROTATIONAL SPECTRA OF THE $v_2 = 1$ AND $v_3 = 1$ STATES

E. A. COHEN, H. S. P. MÜLLER, *Jet Propulsion Laboratory, California Institute of Technology, Pasadena, California 91109*; T. L. TAN, *Department of Physics, Faculty of Science, National University of Singapore, Lower Kent Ridge Road, Singapore 0511, Singapore*; G. A. McRAE, *Atomic Energy of Canada Limited, Chalk River Laboratories, Chalk River, Ontario K0J 1J0, Canada*; J. W. C. JOHNS, *Steacie Institute for Molecular Sciences, National Research Council of Canada, Ottawa, Ontario K1A 0R6, Canada*; and M. NOËL, *Institute for National Measurement Standards, National Research Council of Canada, Ottawa, Ontario K1A 0R6, Canada.*

RG06

15 min 2:45

SPECTROSCOPY OF BROMINE DIOXIDE, OBrO

HOLGER S. P. MÜLLER, CHARLES E. MILLER, and EDWARD A. COHEN, *Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA 91109.*

Intermission

RG07

15 min 3:20

MICROWAVE SPECTRUM AND GEOMETRY OF CYANOGEN N-OXIDE, NCCNO

Th. BRUPBACHER, R. K. BOHN^a, W. JÄGER^b, M. C. L. GERRY, *Department of Chemistry, University of British Columbia, Vancouver, B. C., Canada, V6T 1Z1*; T. PASINSZKI and N. P. C. WESTWOOD, *Department of Chemistry, University of Guelph, Guelph, Ont., Canada, N1G 2W1*.

^aPermanent address: Department of Chemistry, University of Connecticut, Storrs, CT 06269-4060, U.S.A.

^bPresent address: Department of Chemistry, University of Alberta, Edmonton, Alta., Canada, T6G 2G2

RG08

15 min 3:37

RADIO FREQUENCY-INFRARED DOUBLE RESONANCE MEASUREMENT OF THE ELECTRIC DIPOLE MOMENT IN BEND-STRETCH COMBINATION VIBRATIONAL STATES OF HCCD

MARK D. MARSHALL, *Department of Chemistry, Amherst College, Amherst, MA 01002 and Department of Chemistry, University of Rochester, Rochester, NY 14627*; K. CAN IZGI, and J. S. MUENTER, *Department of Chemistry, University of Rochester, Rochester, NY 14627*.

RG09

10 min 3:54

THE JET PROPULSION LABORATORY SUBMILLIMETER, MILLIMETER AND MICROWAVE SPECTRAL LINE CATALOG

HERBERT M. PICKETT, R. L. POYNTER, E. A. COHEN, M. L. DELITSKY, J. C. PEARSON and H. S. P. MÜLLER, *Jet Propulsion Laboratory, California Institute of Technology, Mail Stop 183-301, 4800 Oak Grove Dr., Pasadena, CA 91109*.

RG10

10 min 4:06

MEASUREMENTS OF THE MICROWAVE SPECTRUM, STRUCTURAL PARAMETERS, AND QUADRUPOLE COUPLING FOR METHYL RHENIUM TRIOXIDE

S. M. SICKAFOOSE, P. WIKRENT, B. J. DROUIN, and S. G. KUKOLICH, *Department of Chemistry, University of Arizona, Tucson, AZ 85721*.

RG11

15 min 4:18

MICROWAVE MOLECULAR STRUCTURE MEASUREMENTS FOR TETRACARBONYL DIHYDRO OSMIUM, A CLASSICAL DIHYDRIDE

S. G. KUKOLICH, S. M. SICKAFOOSE, and S. M. BRECKENRIDGE, *Department of Chemistry, The University of Arizona, Tucson, AZ 85721*.

RG12

15 min 4:35

MEASUREMENTS OF THE MICROWAVE SPECTRUM, Co-H BOND LENGTH, AND ⁵⁹Co QUADRUPOLE COUPLING FOR THE TRANSITION METAL HYDRIDE HCo(CO)₄

S. M. SICKAFOOSE and S. G. KUKOLICH, *Department of Chemistry, University of Arizona, Tucson, AZ 85721*.

RG13

10 min 4:52

MILLIMETER AND SUBMILLIMETER SPECTROSCOPY OF CHLORINE NITRATE:
THE CI QUADRUPOLE TENSOR AND THE HARMONIC FORCE FIELD

HOLGER S. P. MÜLLER, *Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA 91109*;
PAUL HELMINGER, *Department of Physics, University of South Alabama, Mobile, AL 36688*; SIDNEY H. YOUNG, *Department of Chemistry, University of South Alabama, Mobile, AL 36688*.

RG14

10 min 5:04

MICROWAVE SPECTRUM, BROMINE NUCLEAR QUADRUPOLE COUPLING CONSTANTS, AND STRUCTURE
OF BROMODIFLUOROMETHANE

TERUHIKO OGATA, SUSUMU KUWANO, *Department of Chemistry, Faculty of Science, Shizuoka University, Shizuoka, 422 Japan*.

RG15

Post-deadline Abstract

15 min 5:16

A NOVEL DESIGN MOLECULAR BEAM FOURIER TRANSFORM MICROWAVE SPECTROMETER IN THE FRE-
QUENCY RANGE 1 TO 4 GHZ

DANIELA CONSALVO, VOLKER STORM, HELMUT DREIZLER, JENS-UWE GRABOW, and ILONA MERKE, *Institut für Physikalische Chemie, Christian-Albrechts-Universität, Olshausenstraße 40-60, D-24098 Kiel, Germany*.

RH. JET AND BEAM

THURSDAY, JUNE 13, 1996 – 1:30 PM

Room: 1008 EVANS LAB

Chair: JAMES COE, The Ohio State University, Columbus, Ohio

RH01 15 min 1:30

DOORWAY STATE ENHANCED INTRAMOLECULAR VIBRATIONAL ENERGY REDISTRIBUTION IN THE ASYMMETRIC ETHYLENIC C-H STRETCH OF *Cis* METHYL VINYL ETHER

DAVID A. MCWHORTER, SAM CUPP, CHUNG YI LEE and BROOKS H. PATE, *Department of Chemistry, University of Virginia, Charlottesville, VA 22901.*

RH02 15 min 1:47

PHOTOFRAGMENT TRANSLATIONAL SPECTROSCOPY OF HYDROGEN BONDED CLUSTERS AND CHARGE TRANSFER COMPLEXES

J. W. BURNETT, G. DEBOER, and M. A. YOUNG, *Department of Chemistry, University of Iowa, Iowa City, IA 52242.*

RH03 15 min 2:04

THE EFFECT OF REDUCED MASS ON CROSSED BEAM ROVIBRATIONAL ENERGY TRANSFER FROM S_1 GLYOXAL (0^0 , $K' = 0$)

S.M. CLEGG, C.S. PARMENTER, *Department of Chemistry, Indiana University, Bloomington, IN 47405;* S.-P. LU, *Innovative Lasers Corp., 3280 East Hemisphere Loop #120, Tucson, AZ 85706.*

RH04 15 min 2:21

VIBRATIONAL ENERGY TRANSFER OF $I_2(X, v=23 \text{ AND } v=43)$ IN A HELIUM FREE JET EXPANSION

T. A. VAN MARTER, W. G. LAWRENCE, and M. C. HEAVEN, *Department of Chemistry, Emory University, Atlanta, GA 30322.*

RH05 15 min 2:38

VIBRATIONAL PREDISSOCIATION OF $Na^+(CH_3OH)_m$ ($m=2-7$) FROM 2.5 TO 3.0 MICRONS.

C. J. WEINHEIMER and J. M. LISY, *Department of Chemistry, University of Illinois at Urbana-Champaign, Urbana, IL 61801.*

RH06 15 min 2:55

VIBRATIONAL PREDISSOCIATION OF $Na^+(CH_3OH)_m((CH_3)_2CO)_n$ ($m + n > 1$; $m, n \geq 1$) FROM 2.5 TO 3.0 MICRONS.

C. J. WEINHEIMER and J. M. LISY, *Department of Chemistry, University of Illinois at Urbana-Champaign, Urbana, IL 61801.*

RH07

15 min 3:12

MEASURING THE NUCLEAR HYPERFINE POPULATIONS IN THE GROUND ELECTRONIC STATE OF ATOMIC HYDROGEN USING VELOCITY-ALIGNED DOPPLER SPECTROSCOPY

K. A. COWEN, K. T. LORENZ, P. E. FLEMING, M. F. HERMAN, and B. KOPLITZ, *Department of Chemistry, Tulane University, New Orleans, LA 70118.*

RH'. INFRARED**THURSDAY, JUNE 13, 1996 – 3:45 PM****Room: 1008 EVANS LAB****Chair: LINDA BROWN, Jet Propulsion Laboratory, Pasadena, California****RH'01** **10 min 3:45**THE HIGH-RESOLUTION SPECTRUM OF WATER VAPOR BETWEEN 11300 AND 13200 CM^{-1}

J.-M. FLAUD, C. CAMY-PEYRET, J.-P. CHEVILLARD, *Universite Pierre et Marie Curie, Paris, France*;
 A. BYKOV, O. NAUMENKO, T. PETROVA, A. SCHERBAKOV, L. SINITSA, *Institute of Atmospheric Optics, 634055 Tomsk, Russia*.

RH'02 **15 min 3:57**THE TORSION-ROTATION SPECTRUM OF D_2O_2

J.-M. FLAUD, *Laboratoire de Physique Moléculaire et Atmosphérique, Université Pierre et Marie Curie et CNRS, 4 place Jussieu, Tour 13, 75252 Paris Cedex, France*; J. W. JOHNS and Z. LU, *Steacie Institute for Molecular Sciences, National Research Council of Canada, Ottawa, Ontario K1A 0R6, Canada*.

RH'03 **15 min 4:14**

THE INFRARED SPECTRUM OF THE NO DIMER

A. R. W. McKELLAR and J. K. G. WATSON, *Steacie Institute for Molecular Sciences, National Research Council of Canada, Ottawa, Ontario K1A 0R6, Canada*.

RH'04 **15 min 4:31**HIGH RESOLUTION INFRARED SPECTRA OF $^{120}SnD_4$

M. HALONEN^a, L. HALONEN^a, *Department of Chemistry, Princeton University, NJ 08544*; H. BÜRGER and W. JERZEMBECK, *FB9- Anorganische Chemie, Universität-GH Wuppertal, D-42097 Wuppertal, Germany*.

^aPermanent address of M. and L. Halonen: Laboratory of Physical Chemistry, P.O. Box 55 (A.I. Virtasen aukio 1), FIN-00014 University of Helsinki, Finland

RH'05 **10 min 4:48**

HIGH RESOLUTION DIODE LASER SPECTROSCOPY OF CARBONYL FLUORIDE AT STRATOSPHERIC TEMPERATURES

GEOFFREY DUXBURY^j, MARK MCPHAIL, *Department of Physics and Applied Physics, Strathclyde University, Glasgow G4 0NG, Scotland, UK*; RANDY MAY, *Jet Propulsion Laboratory, 4800 Oak Grove Drive, Pasadena CA 91107*.

^jvisiting fellow at JILA

RH'06 **15 min 5:00**HIGH RESOLUTION SPECTROSCOPY OF CH_2F_2 IN THE 3 μm REGION. THE $2\nu_8$ BAND AT 2839 CM^{-1}

CATHERINE L. LUGEZ, ALFONS WEBER, and WALTER J. LAFFERTY, *Molecular Physics Division, National Institute of Standards and Technology, Gaithersburg, MD 20899*.

RH'07**15 min 5:17****COROLIS-DEPENDENT DIPOLE MOMENT OF THE $V_3 = 2$ STATE OF METHANE**

H. SASADA, K. SUZUMURA, and C. ISHIBASHI, *Department of Physics, Faculty of Science and Technology, Keio University, Yokohama 223, Japan.*

RH'08**15 min 5:34****RAMAN SPECTROSCOPY OF PHASE TRANSITIONS IN NEMATIC LIQUID CRYSTALS**

I. ESTRELA-LLOPIS, V. POGORELOV, *Department of Physics, Kiev Taras Shevchenko's University, Glushkov pr. 6, Kiev 252127, Ukraine.*

FA. SYMPOSIUM: COHERENT IR

FRIDAY, JUNE 14, 1996 – 8:30 AM

Room: 1153 SMITH LAB

Chair: KEN EVENSON, NIST, Boulder, Colorado

FA01 **INVITED TALK** **30 min 8:30**
INFRARED SOURCES FOR SPECTROSCOPY BASED ON DIFFERENCE FREQUENCY GENERATION

F. K. TITTEL, R. F. CURL, K. PETROV, W. C. ECKHOFF, S. WANG, *Departments of Chemistry and Electrical and Computer Engineering and Rice Quantum Institute, Rice University, Houston, TX 77251*; R. S. PUTNAM, *Aerodyne Research Inc., 45 Manning Road, Billerica MA 01821*; L. HOLLBERG, S. WALTMAN, *Time and Frequency Division, National Institute of Standards and Technology, 325 Broadway, Boulder, Colorado 80303*; L. GOLDBERG, AND W. K. BURNS, *Naval Research Laboratory, Washington, D.C. 20375-5672*.

FA02 **15 min 9:05**
GENERATION AND CONTROL OF SUBMILLIMETER RADIATION WITH LOCKED DBR DIODE LASERS

HERBERT M. PICKETT, J. C. PEARSON and S. DUBOVITSKY, *Jet Propulsion Laboratory, California Institute of Technology, Mail Stop 183-301, 4800 Oak Grove Dr., Pasadena, CA 91109*.

FA03 **15 min 9:22**
FAST SCAN BACKWARD WAVE OSCILLATOR SPECTROMETER

D. T. PETKIE, T. M. GOYETTE, and F. C. DE LUCIA, *Department of Physics, The Ohio State University 174 West 18th Avenue, Columbus, OH 43210-1106*.

FA04 **15 min 9:39**
A FEMTOSECOND DEMODULATION SOURCE FOR HIGH-RESOLUTION SUBMILLIMETER SPECTROSCOPY

T. M. GOYETTE, J. R. DEMERS, W. GUO, *Department of Physics, The Ohio State University, 174 West 18th Avenue, Columbus, OH 43210-1106*; K. JUVAN, J. C. SWARTZ, *Department of Physics, Duke University, Durham NC 27706*; H. O. EVERITT, *U. S. Army Research Office, Research Triangle Park, NC 27709*; E. R. BROWN, *Lincoln Laboratory, Massachusetts Institute of Technology, Lexington MA 02173-9108*; B. D. GUENTHER, *U. S. Army Research Office, Research Triangle Park, NC 27709*; F. C. DE LUCIA, *Department of Physics, The Ohio State University, 174 West 18th Avenue, Columbus, OH 43210-1106*.

FA05 **15 min 9:56**
AN ANALYTIC EXPRESSION FOR THE MOLECULAR EMISSION SIGNAL OBSERVED IN COAXIAL-NOZZLE FOURIER-TRANSFORM MICROWAVE SPECTROSCOPY

J.-U. GRABOW, *Institut für Physikalische Chemie, Christian-Albrechts-Universität, Olshausenstr. 40-60, D-24098 Kiel, Germany*.

Intermission

FA06

INVITED TALK

30 min 10:30

DIODE LASERS AND NONLINEAR OPTICS FOR SPECTROSCOPY, FROM THE UV TO MILLIMETER WAVES

L. HOLLBERG, J. H. MARQUARDT, S. WALTMAN and R. W. FOX, *National Institute of Standards and Technology, 325 Broadway, Boulder, CO 80303.*

FA07

10 min 11:05

NEW LASER LINES AND FREQUENCY MEASUREMENTS OF FULLY DEUTERATED ISOTOPOMERS OF METHANOL

E.C.C. VASCONCELLOS, S.C. ZERBETTO, *Instituto de Fisica Gleb Wataghin, Departamento de Eletronica Quantica, Universidade Estadual de Campinas (UNICAMP), 13083-970, Campinas, SP, Brazil*; L.R. ZINK, and K.M. EVENSON, *National Institute of Standards and Technology, Time and Frequency Division, Boulder, CO 80303-3328.*

FA08

10 min 11:17

OPTICALLY PUMPED FAR-INFRARED LASERS FROM METHANOL ISOTOPOMERS: $^{12}\text{CD}_3\text{OH}$, $^{12}\text{CH}_3\text{OD}$, AND $^{12}\text{CH}_2\text{DOH}$; NEW LASER LINES AND FREQUENCY MEASUREMENTS

E.C.C. VASCONCELLOS, S.C. ZERBETTO, *Instituto de Fisica Gleb Wataghin, Departamento de Eletronica Quantica, Universidade Estadual de Campinas (UNICAMP), 13083-970, Campinas, SP, Brazil*; L.R. ZINK, and K.M. EVENSON, *National Institute of Standards and Technology, Time and Frequency Division, Boulder, CO 80303-3328.*

FA09

15 min 11:29

RECENT WORK IN HIGH RESOLUTION ROVIBRATIONAL SPECTROSCOPY AT THE INSTITUTO DE ESTRUCTURA DE LA MATERIA IN MADRID

JULIO SANTOS, JOSÉ L. DOMÉNECH, RAÚL Z. MARTÍNEZ, DIONISIO BERMEJO, *Instituto de Estructura de la Materia (C.S.I.C), Serrano 123, 28006 Madrid, SPAIN.*

FA10

Post-deadline Abstract

15 min 11:46

NEW EXPERIENCES WITH THE FOURIER TRANSFORM SPECTROMETER IN THE MILLIMETER WAVE RANGE

ANTONIO GUARNIERI, JENS DOOSE, NICO NISSEN, and HEINRICH MÄDER, *Institut für Physikalische Chemie, Christian-Albrechts-Universität, Olshausenstraße 40-60, D-24098 Kiel, Germany.*

FB. INFRARED: JET AND BEAM**FRIDAY, JUNE 14, 1996 – 8:30 AM****Room: 1009 SMITH LAB**

Chair: LI-HONG XU, University of New Brunswick, Saint John, NB, Canada

FB01 **15 min 8:30****COMPREHENSIVE ANALYSIS OF THE IR SPECTRUM OF Ar-CO, INCLUDING INTERMOLECULAR BENDING AND STRETCHING STATES**

YUNJIE XU and A. R. W. McKELLAR, *Steacie Institute for Molecular Sciences, National Research Council of Canada, Ottawa, Ontario K1A 0R6, Canada.*

FB02 **15 min 8:47****SLIT-JET INFRARED SPECTRUM OF THE CO-N₂ COMPLEX**

YUNJIE XU and A. R. W. McKELLAR, *Steacie Institute for Molecular Sciences, National Research Council of Canada, Ottawa, Ontario K1A 0R6, Canada.*

FB03 **15 min 9:04****INFRARED SPECTROSCOPY OF THE Ar-C₂HD COMPLEX: POTENTIAL ENERGY SURFACES**

R. J. BEMISH and R. E. MILLER, *Department of Chemistry, University of North Carolina, Chapel Hill, NC 27599.*

FB04 **15 min 9:21****TWO EXAMPLES OF LONG LIVED METASTABLE SYSTEMS: Ar-HCl (v=1) AND Ar-DF (v=1)**

L. OUDEJANS, B. K. NAUTA and R. E. MILLER, *Department of Chemistry, University of North Carolina, Chapel Hill, NC 27599.*

FB05 **15 min 9:38****FINAL STATE DISTRIBUTIONS UPON VIBRATIONAL PREDISSOCIATION OF THE HCl DIMER**

L. OUDEJANS and R. E. MILLER, *Department of Chemistry, University of North Carolina, Chapel Hill, NC 27599.*

FB06 **15 min 9:55****ISOTOPIC SUBSTITUTION OF A HYDROGEN BOND: A NEAR-IR STUDY OF ALL 4 INTERMOLECULAR MODES IN DF DIMER**

SCOTT DAVIS, DAVID T. ANDERSON, and DAVID J. NESBITT, *JILA, National Institute of Standards and Technology and Department of Chemistry and Biochemistry, University of Colorado, Boulder, CO 80309-0440.*

Intermission

FB07**15 min 10:30****HYDRATED PROTON CLUSTERS**

LARS PEDER OJAMÄE, *Department of Quantum Chemistry, Uppsala University*; SHERWIN J. SINGER, and ISAIAH SHAVITT, *Department of Chemistry, Ohio State University*.

FB08**15 min 10:47****HIGH RESOLUTION INFRARED SPECTROSCOPY OF CO₂-N₂O**

C. DUTTON, A. SAZONOV, R. A. BEAUDET, *Department of Chemistry, University of Southern California, Los Angeles, CA 90089-0482*.

FB09**10 min 11:04****AB INITIO CALCULATIONS OF THE CO₂-N₂O VAN DER WAALS COMPLEX**

A. SAZONOV and R. A. BEAUDET, *Department of Chemistry, University Southern California, Los Angeles, CA 90089-0482*.

FB10**15 min 11:16****ROVIBRATIONAL SPECTROSCOPY AND MOLECULAR DYNAMICS OF Ar-HBr**

J. HAN, A. L. McINTOSH, Z. WANG, R. R. LUCCHESI, and J. W. BEVAN, *Department of Chemistry, Texas A and M University, College Station, TX 77843*.

FB11**15 min 11:33****A ROVIBRATIONAL ANALYSIS OF THE ν_1 AND ν_2 BANDS OF OC-DF BY FTIR SUPERSONIC JET SPECTROSCOPY**

J. HAN, A. L. McINTOSH, C. L. HARTZ, AND J. W. BEVAN, *Department of Chemistry, Texas A and M University, College Station, TX 77843*.

FB12**15 min 11:50****VIBRATIONAL OVERTONE (3-0) SPECTROSCOPY OF Ar₂HF AND Ar₃HF**

CHENG-CHI CHUANG, WILLIAM KLEMPERER, *Department of Chemistry, Harvard University, Cambridge, MA 02138*; HUAN-CHEN CHANG, *Institute of Atomic and Molecular Sciences, Academia Sinica, P.O.Box 23-166, Taipei, Taiwan 10764, Republic of China*.

FC. THEORY

FRIDAY, JUNE 14, 1996 – 8:30 AM

Room: 1005 SMITH LAB

Chair: PETER GRONER, University of Missouri-Kansas City, Kansas City, Missouri

FC01 15 min 8:30
 COORDINATES, HAMILTONIAN AND SYMMETRY OPERATIONS FOR THE SMALL-AMPLITUDE VIBRATIONAL PROBLEM IN INTERNAL-ROTOR MOLECULES LIKE CH₃CHO

JON T. HOUGEN, *Molecular Physics Division, National Institute of Standards and Technology, Gaithersburg, MD 20899.*

FC02 15 min 8:47
 METHYL ROTOR INTRAMOLECULAR DYNAMICS OF GASEOUS NITROMETHANES NO₂CH₃ AND NO₂CH₂D

D. CAVAGNAT, L. LESPADE, *Laboratoire de Spectroscopie Moléculaire et Cristalline, URA 124, 351 crs de la Libération, 33405 Talence, FRANCE.*

FC03 15 min 9:04
 METHYLAMINE TORSIONAL-WAGGING FIR SPECTRUM HNH BENDING ANGLE DEPENDENCE

Y. G. SMEYERS, *Instituto de Estructura de la Materia, C.S.I.C., Calle Serrano, no. 123, 28006 Madrid, Spain*; M. VILLA, *Departamento de Química, U.A.M.-I, Av. La Purisima y Michoacan, CP 09340, Mexico D.F., Mexico*; and M. L. SENENT, *Instituto de Estructura de la Materia, C.S.I.C., Calle Serrano, no. 123, 28006 Madrid, Spain.*

FC04 15 min 9:21
 THEORETICAL STUDY OF VIBRATIONAL OVERTONE SPECTROSCOPY AND DYNAMICS IN METHANOL

L. O. HALONEN and K. K. LEHMANN, *Department of Chemistry, Princeton University, NJ 08544.*

FC05 15 min 9:38
 THE PERPENDICULAR C-H STRETCHING BAND ν_9/ν_{13} AND THE TORSIONAL POTENTIAL OF DIMETHYLACETYLENE

J. PLÍVA, *Department of Physics, Pennsylvania State University, University Park, PA 16802*; A. S. PINE, *NIST, Gaithersburg, MD 20899*; S. CIVIŠ, *J. Heyrovský Institute of Physical Chemistry, Czech Academy of Sciences, 18223 Prague, Czech Republic.*

FC06 15 min 9:55
 AN ADIABATIC MODEL OF THE BENDING DYNAMICS OF ACETYLENE

ANNE B. MCCOY, *Department of Chemistry, The Ohio State University, Columbus, OH 43210.*

Intermission

FC07

15 min 10:30

THEORY OF ODD TORSIONAL TRANSITIONS IN THE $V-N$ RESONANCE RAMAN SPECTRUM OF ETHYLENE

J. K. G. WATSON, W. SIEBRAND, M. Z. ZGIERSKI, *Steacie Institute for Molecular Sciences, National Research Council of Canada, Ottawa, Ontario, Canada K1A 0R6.*; M. PAWLIKOWSKI, *Department of Computational Methods in Chemistry, Jagiellonian University, 30-060 Cracow, Poland.*

FC08

15 min 10:47

PENDULAR STATES AND IVR

G.T. FRASER, *Optical Technology Division, National Institute of Standards and Technology, Gaithersburg, MD 20899*; J. ORTIGOSO, *Inst. Estructura de la Materia, CSIC, Serrano, 119-123, 28006 Madrid, Spain*; B.H. PATE, *Department of Chemistry, University of Virginia, Charlottesville, VA 22901.*

FC09

15 min 11:04

THE CLASSICAL DYNAMICS OF MOLECULES WITH FERMI RESONANCE

MARC JOYEUX, *Laboratoire de Spectrométrie Physique (CNRS UA08), Université Joseph Fourier-Grenoble I, BP 87, 38402 St. Martin d'Hères Cedex, France.*

FC10

15 min 11:21

NATURE OF BARRIER FORCES IN ACETALDEHYDE

D. GUO and L. GOODMAN, *Wright and Rieman Chemistry Laboratories, Rutgers University, New Brunswick, NJ 08903.*

FC11

15 min 11:38

WHERE DOES THE DIMETHYL ETHER INTERNAL ROTATION BARRIER COME FROM?

V. POPHRISTIC and L. GOODMAN, *Wright and Reiman Chemistry Laboratories, Rutgers University, New Brunswick, NJ 08903.*

FC12

15 min 11:55

FERMI RESONANCES AND LOCAL MODES IN XH_3 TYPE PYRAMIDAL AND IN XH_4 TYPE TETRAHEDRAL MOLECULES

L. O. HALONEN, *Department of Chemistry, Princeton University, NJ 08544.*

FC13

Post-deadline Abstract

10 min 12:12

THEORETICAL STUDY OF AVOIDED RESONANCE OVERLAPPING AND TRAPPING EFFECT IN PREDISSOCIATION PROCESSES

M. DESOUTER-LECOMTE, V. BREMS, *Département de Chimie, Université de Liège, B6, Sart Tilman, B-4000 Liège, BELGIUM*; J. LIÉVIN, *Laboratoire de Chimie Physique Moléculaire, Université Libre de Bruxelles, CPI 160/09, B-1050 Bruxelles, BELGIUM.*

FC14

Post-deadline Abstract

10 min 12:24

AB INITIO CALCULATION OF THE PHOTOABSORPTION CROSS SECTION OF NO_2 BY THE TWO-DIMENSIONAL REFLECTION METHOD

A. DELON, B. KIRMSE, R. JOST, *LCMI/CNRS BP166, 38042 Grenoble Cedex 9, France*; J. LIÉVIN, *Laboratoire de Chimie Physique Moléculaire, Université Libre de Bruxelles, CPI 160/09, B-1050 Bruxelles, BELGIUM.*

FD. ELECTRONIC (SMALL)**FRIDAY, JUNE 14, 1996 – 8:30 AM****Room: 1008 EVANS LAB****Chair: JOEL TELLINGHUISEN, Vanderbilt University, Nashville, Tennessee****FD01** **15 min 8:30**MAGNETIC FIELD TUNING OF THE NO₂ PHOTODISSOCIATION THRESHOLD

REMY JOST, ANTOINE DELON, JESPER NYGÅRD and ADAM PASINSKI, *Grenoble High Magnetic Field Laboratory, CNRS, BP 166, 38042 Grenoble Cedex 9, France.*

FD02 **15 min 8:47**PREDISSOCIATION OF RYDBERG STATES OF CO INVESTIGATED BY THE DETECTION OF C(³P_J) FRAGMENT

TAKUMICHI SUTANI, TAKAYUKI EBATA, and NAOHIKO MIKAMI, *Department of Chemistry, Graduate School of Science, Tohoku University, Sendai, 980-77, Japan.*

FD03 **15 min 9:04**

PHOTODISSOCIATION SPECTROSCOPY OF THE MIXED METAL DIMER MgLi

K. R. BERRY and M. A. DUNCAN, *Department of Chemistry, University of Georgia, Athens, GA 30602.*

FD04 **15 min 9:21**PHOTODISSOCIATION SPECTROSCOPY OF Ca⁺(H₂O) AND Ca⁺(D₂O)

C. T. SCURLOCK, S. H. PULLINS, J. E. REDDIC, and M. A. DUNCAN, *Department of Chemistry, University of Georgia, Athens, GA 30602.*

FD05 **15 min 9:38**

PHOTOFRAGMENT SPECTROSCOPY OF HI PHOTODISSOCIATION. 1. DOPPLER SPECTROSCOPY OF THE HYDROGEN FRAGMENT

DENIS J. GENDRON and JOHN W. HEPBURN, *CMBLC, Dept. of Chemistry, University of Waterloo, Ontario, CANADA.*

FD06 **10 min 9:55**

VIBRATIONALLY MEDIATED PHOTODISSOCIATION OF HCN

C. R. BUCHER, B. M. HARVEY and K. K. LEHMANN, *Department of Chemistry, Princeton University, Princeton N. J. 08544.*

Intermission**FD07** **10 min 10:30**

CONCERTED REACTION ON THE TIMESCALE OF MOLECULAR VIBRATIONS

UNA MARVET and MARCOS DANTUS, *Department of Chemistry, Michigan State University, East Lansing, MI.*

FD08**15 min 10:42****FEMTOSECOND PHOTOASSOCIATION SPECTROSCOPY (FPAS)**

UNA MARVET and MARCOS DANTUS, *Department of Chemistry, Michigan State University, East Lansing, MI.*

FD09**15 min 10:59****REACTION OF NFCI_2 WITH ARGON METASTABLES**

YEVGENIYA I. GERHANOVICH, JULANNA G. GILBERT, *Department of Chemistry, University of Denver, Denver, CO 80208.*

FD10**10 min 11:16****AB INITIO CALCULATIONS ON THE PHOTOLYSIS OF CHLORINE NITRATE (ClONO_2)**

L. -Y. CHOW CHIU, *Department of Chemistry, Howard University, Washington DC 20059*; M. H. LIN, *Department of Chemistry, The Catholic University of America, Washington DC 20064*; S. T. LAI, *Vitreous State Laboratory, The Catholic University of America, Washington DC 20064.*

FD11**15 min 11:28****THE EFFECTS OF TRIPLET PERTURBERS ON PHOTOPHYSICAL PROCESSES IN ACETYLENE**

STEPHEN DRUCKER, JONATHAN P. O'BRIEN, PARESH PATEL, and ROBERT W. FIELD, *MIT, 77 Massachusetts Avenue, Cambridge, MA 02139.*

FD12**15 min 11:45****RADIATIVE AND NONRADIATIVE DECAY OF ELECTRONICALLY EXCITED NCO**

SCOTT A. WRIGHT and PAUL J. DAGDIGIAN, *Department of Chemistry, The Johns Hopkins University, Baltimore, MD 21218-2685.*

FD13*Post-deadline Abstract***15 min 12:02****ZEKE-PFI SPECTROSCOPY OF THE SODIUM-WATER AND SODIUM-AMMONIA DIMERS**

GEOFFEREY A. BLAKE and DAVID A. RODHAM, *Division of Geological and Planetary Sciences California Institute of Technology MS 170-25 Pasadena, CA 91125.*

MA01**40 min 9:00****SPECTROSCOPY AND DYNAMICS OF HIGH SPIN ALKALI OLIGOMERS¹**

G. SCOLES, Department of Chemistry, Princeton University, Princeton, NJ 08544.

A beam of large helium clusters, made each of approximately 10^4 atoms, is used to "matrix isolate" high spin alkali dimers and trimers. The high spin triplet and quartet states formed on the clusters survive preferentially over their singlet and doublet counterparts. The large energy liberated by the low spin species upon formation will destroy a larger fraction of the host clusters. Total and dispersed fluorescence studies have allowed the recording of several previously unobserved alkali dimer triplet to triplet transitions and the first quartet to quartet transition of the Na trimer. The results indicate that the Hartree-Fock plus damped Dispersion interatomic potential model (HFD) accurately describes the interactions in the lowest alkali triplet states and provide information on the (strong) presence of three body forces in the interaction of three spin-polarized alkali atoms.

¹ Work carried out in collaboration with C. Callegari, W. E. Ernst, M. Gutowski, J. Higgins, K. K. Lehmann, J. Reho, and F. Stienkemeier with the financial support of AFOSR and the German Research Foundation (DFG).

MA02**40 min 9:45**

SPECTROSCOPY OF DIATOMIC TRANSITION METAL MOLECULES, M.D.MORSE, Department of Chemistry, University of Utah, Salt Lake City, UT 84112.

Resonant two-photon ionization spectroscopy of jet-cooled diatomic transition metal molecules has been actively pursued in this laboratory for the past 10 years. In this plenary lecture results on the nickel and copper group diatomics will be presented. The spectra of the copper group diatomics (Cu_2 , Ag_2 , Au_2 , CuAg , CuAu , and AgAu) are used to illustrate the general importance of ion-pair states as sources of oscillator strength in diatomic metals. The nickel group diatomics (Ni_2 , NiPt , and Pt_2) and other open d subshell metal dimers are used to demonstrate how predissociation thresholds in these molecules provide a measure of the bond dissociation energy which is accurate to a few wave numbers. Finally, NiCu , Ni_2 , and AlNi are examined from the framework of a ligand field model in which the metal atoms are taken as possessing an effective +1 charge. This model is demonstrated to reproduce the results of *ab initio* calculations on NiCu and Ni_2 to uncanny accuracy, and to accurately predict the experimentally determined ground states of NiCu , NiAu , AlNi , PtCu , and Ni_2 . Dispersed fluorescence studies on AlNi are compared to the predictions of the ligand field model.

Intermission**MA03****40 min 11:10****Single Molecule Spectroscopy and Chemical Dynamics at Room Temperature**

X. Sunney Xie, *Pacific Northwest National Laboratory, Environmental Molecular Sciences Laboratory, Richland, WA 99352.*

Recent advances in near-field and confocal fluorescence microscopy have made it possible to conduct spectroscopic measurements on single molecules in ambient environments. On the millisecond to minute time scale, single molecule trajectories of conformational motions and spectral fluctuations can be directly recorded. On the picosecond to nanosecond time scale, repetitive processes of single molecules, such as photo-induced chemical reactions, can be studied in specific local environments. We are applying the techniques to study electron transfer and energy transfer processes at interfaces as well as on photosynthetic membranes. These studies illustrate the unique and detailed information obtainable from the single molecule experiments.

ME01**30 min 1:30****CAVITY RINGDOWN SPECTROSCOPY: A LOOK INSIDE THE CAVITY**

Anthony O'Keefe, Los Gatos Research
1685 Plymouth Street, Mountain View CA 94043

The technique of Cavity Ringdown Laser Absorption Spectroscopy (CRLAS) has experienced rapid growth in recent years, both in terms of users as well as the range of applications. The technique offers exceptional versatility in use, resulting from the simplicity of execution. In this talk I will review the early development of the technique, providing a connection between where it came from and where it might go in the future. Present applications ranging from the ultra violet to the mid-infrared will be discussed, with emphasis on the developments in the infrared region. The difficulties and advantages of working in the infrared will be discussed. Limitations caused by the lack of easily tuned pulsed light sources, background absorptions, and by mirror reflectivities, will be considered.

Finally, recent speculation on the role that frequency interference plays in the ringdown process will be discussed. This will include a discussion of the limitations imposed by coherent interference as well as how other non-linear interactions could potentially improve performance in some applications.

ME02**15 min 2:05****The Superposition Principle of Optics and Cavity Ring Down Spectroscopy**

K. K. Lehmann, Department of Chemistry, Princeton University, Princeton N. J. 08544; D. Romanini, Laboratoire de Spectrométrie Physique - CNRS URA 08, Université J. Fourier/Grenoble, B.P. 87 - 38402 Saint Martin d'Hères Cedex, France.

Cavity Ring Down Spectroscopy is an important new spectroscopic tool that promises to be widely useful to gas phase spectroscopists. Unfortunately, the literature is rife with misstatements about spectrum of light inside the ring down cavity. These have arose from the belief that excitation of an optical resonator with a pulse of short coherence length is inherently a complex physical process that is difficult to describe. In this talk, we will demonstrate that the ring down cavity cell can be viewed as a high finesse etalon, and the spectrum of light that enters the cavity is confined to narrow Lorentzian lines near each cavity resonance. This result follows naturally from the superposition principle of optics, and is independent of the coherence properties of the input light, which only effect the distribution of cavity modes which are excited. A consequence of the strong filtering of light that enters the ring down cavity is that it should be possible, using a conventional single mode pulsed laser of a few nsec duration (and thus ~ 300 MHz linewidth) to obtain spectra with much high resolution, limited only by the time of flight of molecules through the focus of the laser beam, which will be ~ 1 MHz in most cases. In order to realize this advantage of cavity ring down, one will need to carefully control the matching of both the spatial and spectral modes of the cavity with the excitation laser. Expressions have been derived that allow the straightforward calculation of the excitation intensity of each cavity mode.

ME03

15 min 2:22

A FOURIER TRANSFORM CAVITY RING DOWN SPECTROMETER

RICHARD ENGELN AND GERARD MEIJER, *Dept. of Molecular and Laser Physics, University of Nijmegen, Toernooiveld, 6526 ED Nijmegen, The Netherlands.*

A novel multiplex absorption spectrometer will be presented, in which the sensitivity of the Cavity Ring Down absorption detection technique is combined with the multiplex advantage of a Fourier Transform spectrometer ^a. A description of the Fourier Transform - Cavity Ring Down (FT-CRD) spectrometer, substantiated with first experimental results on the atmospheric band of molecular oxygen, will be given. The molecular oxygen spectrum, has a noise-equivalent absorption detection limit of $2.5 \cdot 10^{-7} \text{ cm}^{-1}$, corresponding to an $1/e$ absorption length of 40 km, for the present experimental setup. This absorption detection limit even compares favourably to the detection limit that can be obtained using standard continuous FT spectroscopy in a long path-length absorption cell, although then digitizers with a higher dynamic range are used. If interfaced to pulsed, repetitive sources many orders of magnitude are gained in absorption detection sensitivity with the FT-CRD technique compared to presently available FT spectroscopic techniques.

It is demonstrated that as in the case of 'normal' CRD spectroscopy, in a FT-CRD spectrometer the absorption information is deduced from the temporal shape of the ring down transient, and therefore only the spectral shape of the light source has to be known and has to be constant during the measurement, whereas the intensity of the light source is allowed to fluctuate. Since one does not need to know the absolute intensity of the interferograms, less stringent restrictions are posed on the vertical resolution of the digitizer.

Full advantage of the multiplex approach to spectroscopy is obtained in the (near)-IR spectral region where the intrinsic noise level of the light detectors is higher than in the visible and near-UV range. As also the Michelson interferometers work better for longer wavelengths, it is anticipated the the FT-CRD technique that will be presented, is ideal for exploration in the spectroscopically valuable IR region of the spectrum.

^aRichard Engeln and Gerard Meijer, submitted to Rev. Sci. Instrum.

ME04

15 min 2:39

DIRECT-ABSORPTION OBSERVATION OF A DOUBLY-FORBIDDEN ELECTRONIC TRANSITION IN DIACETYLENE USING CAVITY RING-DOWN SPECTROSCOPY

B. GILES, C. A. ARRINGTON, F. C. HAGEMEISTER, AND T. S. ZWIER, *Department of Chemistry, Purdue University, West Lafayette, IN 47907-1393.*

The nominally $^3\Delta_u \leftarrow X^1\sigma_g^+$ transition in room-temperature diacetylene has been observed by direct absorption for the first time using the cavity ring-down technique pioneered by O'Keefe and Deacon ^a. Using mirrors with high reflectivity (99.85%) the wavelength range 396 nm - 342 nm was investigated. Two bands at 27090 cm^{-1} and 27430 cm^{-1} are observed which show a red shading consistent with a $\pi^* \leftarrow \pi$ transition. Band contours also suggest a linear to bent electronic excitation. The largest spectral feature has a measured molar absorption coefficient of $1.5 \times 10^{-4} \text{ L mol}^{-1} \text{ cm}^{-1}$. The $^3\Delta_u$ state is one of the states thought to be responsible for photochemical reactivity.

^aA. O'Keefe and D. A. G. Deacon, Rev. Sci. Instrum. 59, 2544 (1988).

ME05

15 min 2:56

INFRARED CAVITY RINGDOWN LASER ABSORPTION SPECTROSCOPY (IR-CRLAS) OF JET-COOLED WATER CLUSTERS, J.B. PAUL, C.P. COLLIER, AND R.J. SAYKALLY, Department of Chemistry, University of California, Berkeley, CA 94720, J.J. SCHERER, Sandia National Laboratories, Livermore, CA 94551.

We have recently extended the Cavity Ringdown Laser Absorption Spectroscopy technique^{1,2} into the infrared.³ Studies in the 3.0 μm region of water clusters in molecular jets have found two vibrationally resolved bands centered at $3356 \pm 1 \text{ cm}^{-1}$ and $3400 \pm 3 \text{ cm}^{-1}$, which have been previously assigned to the water pentamer and tetramer, respectively. Additionally, we observe a broad continuum absorption exhibiting long range structure, attributable to an inhomogeneously broadened OH-stretch excitation in large water clusters. This feature exhibits similarities with spectra of large water polymers found in cryogenic matrices, and with the infrared absorption of bulk amorphous ice.

¹J.J. Scherer, J.B. Paul, C.P. Collier, and R.J. Saykally, *J. Chem. Phys.* 102, 5190 (1995).

²J.B. Paul, J.J. Scherer, C.P. Collier, and R.J. Saykally, *J. Chem. Phys.* 104, 2782 (1996).

³J.J. Scherer, D. Voelkel, D.J. Rakestraw, J.B. Paul, C.P. Collier, R.J. Saykally, and A. O'Keefe, *Chem. Phys. Lett.* 245, 273 (1995).

ME06

15 min 3:13

Infrared Cavity Ringdown Laser Absorption Spectroscopy (IR-CRLAS) in Low Pressure Flames; J.J. Scherer and D.J. Rakestraw, Combustion Research Facility, Sandia National Laboratories (M/S 9055), Livermore, CA 94551

We have employed Infrared Cavity Ringdown Laser Absorption Spectroscopy¹ (IR-CRLAS) as a diagnostic tool for combustion chemistry studies. High resolution rovibrational absorption spectra have been obtained in low pressure laminar flames in the mid-infrared employing a pulsed single mode optical parametric oscillator (OPO) laser system. The high sensitivity and generality of IR-CRLAS for combustion studies is demonstrated in a variety of flames and is shown to be robust even in sooting environments with high temperature gradients. The ability to obtain spatially resolved data is also demonstrated in one dimensional laminar flame studies. These preliminary results indicate the potential of IR-CRLAS as a combustion diagnostic which is capable of obtaining absolute concentrations of reactants, intermediates, and products simultaneously within a narrow spectral region. In this demonstration, two information rich mid-infrared spectral regions (1.6 and 3-4 microns) have been probed at Doppler-limited resolution with an effective laser bandwidth of $< 0.007 \text{ cm}^{-1}$.

1. J.J. Scherer, D. Voelkel, D.J. Rakestraw, J.B. Paul, C.P. Collier, and R.J. Saykally, *Chem. Phys. Lett.* 245, 273 (1995) This work is supported by the Basic Energy Sciences division of the Department of Energy

ME07

15 min 3:30

QUANTITATIVE ABSORPTION MEASUREMENTS USING CAVITY RING DOWN SPECTROSCOPY

R.D. van Zee, J.P. Looney, J.T. Hodges, *Process Measurements Division, National Institute of Standards and Technology, Gaithersburg, MD 20899.*

This paper investigates the effects of cavity design and laser bandwidth on quantitative cavity ring-down spectroscopy using the 7R transitions of the $X(v=0)$ to $b(v=0)$ band of molecular oxygen. It is found that failure to account for laser bandwidth leads to systematic errors in the number densities determined from measured ring-down signals. By fitting the frequency integrated expression for the ring-down signal and using the measured laser lineshapes, excellent agreement between measured and predicted number densities is found. The quantitative measurement of gas densities over a wide dynamic range will be presented.

ME08

10 min 4:00

Laser Absorption Spectroscopy of TiCl^+ : Analysis of the $[17.9]^3\Delta-X^3\Phi(0,0)$ Band

L. A. Kaledin, J. P. Parrish, and M. C. Heaven, *Department of Chemistry, Emory University, Atlanta, GA 30322*.

The laser absorption spectrum of the TiCl^+ molecular ion was observed for the first time in a hollow cathode discharge. The discharge was driven at 25 kHz at powers in the range of 80-100 W. Peak currents of 0.5 A occurred during the conducting half-cycles. Flowing samples of TiCl_4 in Ar were discharged. 235 lines of the $^{48}\text{Ti}^{35}\text{Cl}^+$ $[17.9]^3\Delta-X^3\Phi(0,0)$ band and 122 lines of the $^{48}\text{Ti}^{37}\text{Cl}^+$ $[17.9]^3\Delta-X^3\Phi(0,0)$ band were recorded at resolution 0.02 cm^{-1} . This band system was observed previously ^a in the emission spectrum of TiCl^+ but the electronic assignments for the lower and upper states of the transition are revised here. Rotational constants (in cm^{-1}) and internuclear distances r_0 (in nm) for the $[17.9]^3\Delta(v=0)$ and $X^3\Phi(v=0)$ states of $^{48}\text{Ti}^{35}\text{Cl}^+$ and $^{48}\text{Ti}^{37}\text{Cl}^+$ are respectively:

$$B'_0 = 0.178692(16), r'_0 = 0.2160(1), B''_0 = 0.174212(16), r''_0 = 0.2188(1), \\ B'_0 = 0.173076(18), r'_0 = 0.2160(1), B''_0 = 0.168742(18), r''_0 = 0.2188(1).$$

These results are in excellent agreement with the predictions based on the ligand field theory models ^b. The symmetry for the ground state of the TiCl^+ molecular ion is determined to be $X^3\Phi$. Work supported by AFOSR under grant F19628-90-C-025.

^aW. J. Balfour and K. S. Chandrasekhar, *J. Mol. Spectrosc.* 139, 245-252 (1990).

^bL. A. Kaledin, J. E. McCord, and M. C. Heaven, *J. Mol. Spectrosc.* 173, 499-509 (1995).

ME09

15 min 4:12

DOUBLE MODULATION TECHNIQUE IN PULSED JET EXPERIMENTS: MOLECULAR VAN DER WAALS COMPLEXES

I. PAK, M. HEPP, D. ROTH, AND G. WINNEWISSER, *I. Physikalisches Institut, Universität zu Köln, 50937 Köln, Germany*.

A double modulation technique was used to achieve higher sensitivity in absorption measurements with a pulsed supersonic jet. The wavelength of a lead-salt diode laser was modulated at a frequency of 10 kHz and detected at twice the frequency by a lock-in amplifier, reducing significantly the influence of the low frequency excess laser noise. The output of this lock-in amplifier was measured by a boxcar integrator, driven at 80 Hz, the frequency of the pulsed jet. The same technique was applied to the jet absorption measurements in the millimeter wave region using mm-wave synthesizers as radiation sources. The recorded spectra of Ar-CH_4 , Kr-CH_4 and Ar-CO molecular van der Waals complexes are presented in order to show the improved sensitivity of the tunable diode laser and mm-wave spectrometers.

ME10**15 min 4:29****Resonant four-wave mixing probes of jet-cooled polyatomic molecules:
Infrared degenerate four wave mixing and Infrared/Visible laser induced
grating spectroscopies**

S. A. Reid and Y. Tang
Department of Chemistry
Marquette University
Milwaukee, WI 53201-1881

ABSTRACT

Resonant four-wave mixing techniques have recently emerged as powerful new tools in molecular spectroscopy. These methods feature an "absorption-like" response that is typically background- and Doppler-free. In this work, we report on our initial studies concerning the application of resonant four-wave mixing techniques in the infrared for the generation of "absorption-like" spectra of jet-cooled polyatomic molecules. In particular, we report on the development and characterization of: (i) infrared degenerate four-wave mixing (DFWM), and (ii) double resonance infrared/visible laser induced grating (LIGS) spectroscopies. We will compare our experimental results to current theoretical models.

ME11**10 min 4:46****High Sensitivity Detection of Trichloroethylene Using Frequency-Modulated Tunable Diode Lasers**

Chi Kong Ng, Khosrow Namjou, Edward A. Whittaker, *Department of Physics and Engineering Physics, Stevens Institute of Technology, Hoboken, NJ 07030.*

There is strong interest in the remote sensing community for high sensitivity optical sensors capable of distinguishing between various volatile organic compounds. In an effort to meet this need we have applied frequency-modulation technique absorption spectroscopy using tunable lead salt diode lasers to detect the compound trichloroethylene. Detection was accomplished using the relatively strong band at 1250cm^{-1} . While detection of a low pressure vapor was relatively straightforward, line blending in atmospheric pressure broadened samples causes much reduced sensitivity. We discuss possible approaches to solving this problem as well some specific details of our frequency modulation techniques which help to optimize achievable sensitivity.

ME12**15 min 4:58****INTRACAVITY SATURATED ABSORPTION SPECTROSCOPY OF THE 1.6-MICRON MOLECULAR OVERTONE BAND**

H. SASADA, AND K. SUZUMURA, *Department of Physics, Faculty of Science and Technology, Keio University, Yokohama 223, Japan.*

Saturation spectroscopy of the $2\nu_3$ band of methane was carried out using an optical cavity absorption cell and a 1.6- μm -grating feedback external-cavity semiconductor laser. An experimental setup was similar with the pioneering work ^a in the 1.5- μm region. Since the linewidth of the observed saturation dips was just 0.5 MHz, a high potential exists for the use of this technique for high resolution spectroscopy and double-resonance spectroscopy.

^aM. de Labachellerie, K. Nakagawa, and M. Ohtsu, *Opt. Lett.* 20, 410 (1994).

ME13**10 min 5:15****PRESSURE BROADENING OF THE O₂ B BAND MEASURED BY CAVITY RING-DOWN SPECTROSCOPY**

D. C. ROBIE, N. SEISER, *Department of Chemistry, Barnard College, New York, NY 10027.*

We have used cavity ring-down spectroscopy to measure pressure-broadening coefficients for several rotational lines in the atmospheric B band of O₂ at 688 nm. Collisional partners of the O₂ include O₂, N₂, and Ar. Total pressures range up to 2 atm; at that pressure, the self-broadened linewidth is 0.3 cm⁻¹, about twice the laser bandwidth. Comparisons with previous measurements by other techniques will be discussed.

ME14**10 min 5:27****APPLICATION OF THE CAVITY RING-DOWN TECHNIQUE TO WATER VAPOUR CONTINUUM MEASUREMENTS**

JOHN G. CORMIER AND JAMES R. DRUMMOND, *Department of Physics, University of Toronto, 60 St. George Street, Toronto, Ont., Canada, M5S 1A7.*

The water vapour "continuum" is a weak and unstructured absorption which spans the infrared spectrum. In the 8-13 μm atmospheric window it is a major factor in the radiative transfer of the lower atmosphere to space, and therefore has implications in the area of climate change. Theoretical models of the water vapour continuum are based on data which contain uncertainties and are sometimes inconsistent. The major reasons for this are the small size of the absorption coupled with the low saturated vapour pressure of water at atmospheric temperatures, which limits the total absorption in any conceivable laboratory path.

Recognising the need for improved continuum measurements, we are currently developing a cavity ring-down experiment, in order to study the water vapour continuum. This paper will discuss the design of the experiment, the expected performance, and the manner by which an acceptable signal-to-noise ratio can be obtained.

MF01

15 min 1:30

HYPERFINE STRUCTURE IN THE MICROWAVE SPECTRUM OF NF_3

STEWART E. NOVICK, WEI CHEN, AND MICHAEELEEN R. MUNROW, Department of Chemistry, Wesleyan University, Middletown, CT 06459; KIMBERLEY J. GRANT, Department of Chemistry, College of Saint Elizabeth, Morristown, NJ 07960

The $J = 1 - 0$ rotational transition of $^{14}\text{NF}_3$ has been measured in high resolution in a pulsed jet Fourier transform microwave spectrometer. The transition is split into three major components due to the nuclear quadrupole coupling constant of the ^{14}N nucleus which in turn is further split into hyperfine components due to the fluorine spin - molecular rotation interaction. The improved values of the rotational and nitrogen quadrupole constants are $A = B = 10681.0819(15)$ MHz and $\chi_{\text{cc}}(\text{N}) = -7.093(8)$ MHz. The newly measured spin-rotation and spin-spin constants are $C_F = 21.8 \pm 1.6$ kHz, $C_N = 2.4 \pm 1.6$ kHz, and $D_{\text{cc}}(\text{F}) = 17 \pm 10$ kHz.

MF02

15 min 1:47

ROTATIONAL SPECTRA OF THE EXCITED VIBRATIONAL STATES OF NITRIC ACID.

T. M. GOYETTE, L. H. COUDERT, L. C. OESTERLING, D. T. PETKIE, R. A. BOOKER, P. HELMINGER, AND F. C. DE LUCIA

All of the fundamentals of nitric acid have now been studied by high resolution infrared techniques. Additionally, the pure rotational spectrum of many of the excited states have been studied by millimeter/submillimeter spectroscopy. However, the analysis for many of the higher vibrational states are not complete. This is in part due to strong Fermi interactions involving interacting dyads such as $\nu_5-2\nu_9$ and $\nu_3-\nu_4$ which make the analysis much more complex. We have recently studied the $\nu_5-2\nu_9$ Fermi interacting bands which also involve torsional effects. The $2\nu_9$ torsional motion produces a large (~ 50 MHz) splitting. Since the $2\nu_9$ vibrational state interacts with the ν_5 vibrational state via Fermi resonance, a large splitting is also induced on the ν_5 energy levels. We have analyzed over 1000 rotational transitions from $\nu_5-2\nu_9$ using two models. The first uses 2 sets of $2\nu_9$ rotational constants and 1 set of ν_5 rotational constants coupled together by Fermi interactions, where a large Fermi term couples the torsional splitting from $2\nu_9$ to ν_5 . The second uses a high barrier IAM approach to account for the torsional splitting. The results of both analyses will be presented as will preliminary results of higher vibrational states.

Address of Goyette, Oesterling, Petkie, and De Lucia: Department of Physics, The Ohio State University, 174 West 18th Avenue, Columbus, OH 43210-1106.

Address of Helming: Department of Physics, University of South Alabama, Mobile, AL 36688.

Address of Coudert: Laboratoire de Physique Moléculaire et Applications, CNRS, Université Pierre et Marie Curie, Cas Courrier 76, Tour 13, 4 Place Jussieu, F-75252 Paris Cedex 05, France.

Address of Booker: Department of Physics, University of North Carolina Asheville, 1 University Heights, Asheville, North Carolina 28804.

MF03

15 min 2:04

MICROWAVE SPECTRA OF NaBH_4 AND KBH_4 IN EXCITED VIBRATIONAL STATES, Y. KAWASHIMA, Department of Chemical Technology, Kanagawa Institute of Technology, Atsugi, Kanagawa 243-02, Japan, E. HIROTA, The Graduate University for Advanced Studies, Hayama, Kanagawa, 240-01, Japan, O.N.ULENIKOV AND A.B. Malikova, Physics Department, Tomsk State University, 634050, Tomsk, Russia.

We have observed two sets of vibrational satellites for each of NaBH_4 and KBH_4 and have assigned them to the non-degenerate alkali metal-boron stretching state and to the degenerate BH_4 bending (or internal rotation) state. The observed transitions were $J=11 \leftarrow 10$ up to $J=20 \leftarrow 19$ and $J=21 \leftarrow 20$ up to $J=28 \leftarrow 27$ for the two molecules, respectively. The satellites of NaBH_4 are quite anomalous; the set of the non-degenerate state extends to higher frequency as K increases, whereas the other set of the degenerate state spreads to lower frequency somewhat more widely than the ground spectrum does. We have analyzed both sets of the vibrational satellites simultaneously using C_{3v} symmetric-top rotational wavefunctions as bases and a vibration-rotation Hamiltonian.^a In the case of NaBH_4 , a strong Coriolis interaction was found to affect even small K levels and allowed us to determine not only B , D_J , D_{JK} , and other minor constants, but also the A rotational constants, the difference between the two band origins W , and the second-order and the first-order Coriolis interaction parameters. On the other hand, the Coriolis interaction perturbed only high- K states of KBH_4 , and thus the A rotational constants and the first-order Coriolis coupling constant could not be derived from the observed spectrum. Therefore, these constants were fixed to *ab initio* values in the analysis. In addition, D_{JK} of the A state was found to strongly correlate with W . The standard deviation of the fit was, or even smaller than, 0.13 and 0.17 MHz, respectively, for NaBH_4 and KBH_4 . A part of this work was supported by RFFR (Pr.N95-03-08081a).

^a Y.Kawashima and E.Hirota, J.Mol. Spectrosc. **153**, 466 (1992).

MF04

15 min 2:21

ROTATIONAL SPECTRUM, STRUCTURE AND DIPOLE MOMENT OF DESFLURANE, R. D. SUENRAM, A. R. HIGHT WALKER, and F. J. LOVAS, Optical Technology Division, NIST, Gaithersburg, MD 20899;

There has been some interest from the medical community in using a portable Fourier-transform microwave (FTMW) spectrometer as a continuous, real-time monitor for the level of an anesthetic that a patient is respiring during surgical procedures. A number of the anesthetics currently in use are volatile halogenated ethers which makes them quite amenable to analysis via the FTMW technique. In order to demonstrate that FTMW spectroscopy can be used for this application, the rotational spectrum of the anesthetic desflurane (1,2,2,2 tetrafluoroethyl difluoromethyl ether, $\text{CF}_3\text{CFHOCF}_2\text{H}$) has been observed and analyzed via FTMW spectroscopy. This chemical is similar to E-245, an alternative refrigerant, (2,2,2 trifluoroethyl difluoromethyl ether, $\text{CF}_3\text{CH}_2\text{OCF}_2\text{H}$) which was reported on in a previous meeting^a. Unlike E-245 which has a symmetry plane, desflurane is chiral and has no symmetry. Spectroscopically it is a more challenging problem since all three selection rules can occur. Furthermore the conformational structure is important since the pure enantiomers have been shown to have different effectiveness^b which led to the suggestion that stereospecific binding between brain proteins and the anesthetic agent might occur. A comparison of the derived structure with the structure obtained using vibrational circular dichroism will be made.^c

^aR. D. Suenram, F. J. Lovas, R. K. Bohn, D. O'Neil and D. Dixon, Talk RE06, 48th International Symposium on Molecular Spectroscopy, 1993.

^bN. P. Franks and W. R. Lieb, Science, **254**, 427-430 (1991).

^cP. L. Polavarapu, Spectroscopy, **9**, 48-55 (1994).

MF05

15 min 2:38

MW AND FTFIR TRANSITIONS OF $^{13}\text{CH}_3\text{OH}$ REVISITED AND REVIEW OF MW SPECTRA OF CH_3OH AND $^{13}\text{CH}_3\text{OH}$ OF ASTROPHYSICAL INTEREST, LI-HONG XU, Department of Physical Sciences, University of New Brunswick, Saint John, N.B., Canada E2L 4L5; M.S. WALSH AND R.M. LEES, Department of Physics, University of New Brunswick, Fredericton, N.B., Canada E3B 5A3; F.J. LOVAS, Radiometric Physics Division, National Institute of Standards and Technology, Gaithersburg, MD 20899

Microwave (MW), millimeter-wave (MMW) and Fourier-transform far-infrared (FTFIR) transitions in the first two torsional states ($v_t = 0$ below the barrier and $v_t = 1$ straddling the barrier) of the ground vibrational state of C-13 methanol have been globally treated and successfully fitted to within assigned measurement uncertainties using a program (I. Kleiner and M. Godefroid private communication) originally designed for acetaldehyde (CH_3CHO) based on the formalism of Herbst *et al.* (*J. Mol. Spectrosc.* **108**, 42-57, 1984). The $^{13}\text{CH}_3\text{OH}$ data set ($v_t \leq 1$, $J \leq 20$, $K_{\text{max}} \leq 14$) contains 725 MW and MMW lines, assigned a ± 50 kHz measurement uncertainty apart from a few K -doublet lines, and 6283 FTFIR lines each assigned an uncertainty of $\pm 0.0002 \text{ cm}^{-1} = \pm 6 \text{ MHz}$. A very satisfactory convergent fit has been achieved using 55 adjustable and 2 fixed parameters, yielding an overall weighted standard deviation of 0.962. Calculations employing the parameters from our final fit reveal possible C-13 assignments for 28 lines appearing in natural abundance in the newly-measured methanol microwave atlas from 7 to 200 GHz compiled by the group of K. Takagi at Toyama university.

The present C-13 work together with the previous global fitting for CH_3OH (*J. Mol. Spectrosc.* **169**, 396-409, 1995, and **173**, 540-551, 1995) set the groundwork for a critical review of the available MW and MMW spectra of CH_3OH and its most abundant isotopomer, $^{13}\text{CH}_3\text{OH}$, for astrophysical application. This review includes frequency calculations based on our torsion-rotation analyses with line uncertainties estimated from the variance-covariance matrices, along with the original references for observed lines. The primary objective of the review is to provide radio astronomers with complete spectral coverage of rotational transitions from 500 MHz to 1 THz, including the lower state energy and line strength for each transition, over the range in rotational quantum number J from 0 to 26.

MF06

15 min 2:55

METHANOL AS A FLEXIBLE MODEL

MIRZA A. MEKHTIEV^a, PETER D. GODFREY, *Chemistry Department, Monash University, Clayton, Victoria 3168, Australia*; VIKTOR SZALAY, *Research Laboratory for Crystal Physics, Hungarian Academy of Sciences, 1502 Budapest, Pf. 132, Hungary*.

A method based on the semi rigid bender and the flexible model approaches has been developed for the internal rotation motion in methanol. For construction of the torsion Hamiltonian matrix a K -dependent trigonometric variational basis set adapted to C_{3v} symmetry was employed. Functions of molecular geometry parameters were chosen as a Fourier series in the torsional angle ρ allowing geometry relaxation of both the top and the frame during the revolution of the top. It was found that when considering certain idealized cases of structure variation with torsional angle, an unusual splitting of the A_1 and A_2 energy levels occurs in the extreme case of a free rotor.

It was shown how the results of the *ab initio* calculations for $C_{3v}(\text{M})$ -molecules could be linked to the developed flexible model by using the approximation of equality of the torsional angle ρ and the average of the three top-frame dihedral angles τ_{eff} .

An analysis of the process of determining the methanol molecular geometry employing the developed model was performed. Two of the zero-order parameters were fixed at the values obtained from electron diffraction measurement and the remaining zero-order parameters and some of the parameters describing variation of the geometry during the torsion as well as the potential energy function were determined for various J_{max} . The fitted values for the bending semirigidity parameters were found to be broadly consistent with those from the MO calculations, whilst the fitted bond stretching parameters were generally in poor agreement.

Line strength calculations have also been performed using the wave functions of various Hamiltonians. It was confirmed that the main contribution to the line strengths comes from the permanent components of the dipole moment whilst the dipole variation with torsion produces little contribution to the methanol line strengths.

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MF07

15 min 3:12

APPLICATIONS OF EFFECTIVE ROTATIONAL HAMILTONIANS FOR TWO-ROTOR MOLECULES

Peter Groner, *Department of Chemistry, University of Missouri - Kansas City, Kansas City, MO 64110.*

Effective rotational Hamiltonians for molecules with one periodic internal motion have been described a few years ago ^a. The same paper also outlined the extension of the model to molecules with more than one periodic motions. Such a Hamiltonian was recently implemented in a computer program to analyze spectra of two-rotor molecules such as CH₃OCH₃ and CH₃COCH₃. Because the analysis was not completely satisfactory, the theoretical treatment was modified producing a different effective rotational Hamiltonian for such molecules. It was subsequently applied, with better success, to the analysis of the same spectra. For the ground state of CH₃OCH₃, 232 rotational transition frequencies of all symmetry species taken from the literature could be fit to an effective rotational Hamiltonian containing 16 parameters, among them 4 internal rotation or tunneling parameters, to yield a standard deviation of 60 kHz; however, about 20 assigned transition frequencies had to be excluded from the fit. Detailed results for the ground and vibrational excited states of CH₃OCH₃, for the ground state of CH₃COCH₃, and for other examples, will be given in the presentation.

^aP. Groner, *J. Mol. Spectrosc.* 156, 164-189 (1992).

Intermission

MF08

15 min 3:45

THE SUBMILLIMETER SPECTRUM OF THE GROUND HYDROXYL TORSIONAL STATE OF ETHYL ALCOHOL (CH₃CH₂OH)

J. C. PEARSON, *Jet Propulsion Laboratory, California Institute of Technology, Mail Stop 183-301, 4800 Oak Grove Dr., Pasadena, CA 91109*; K. V. L. N. SASTRY, *Department of Physics, University of New Brunswick, Fredericton, New Brunswick, E3B 5A3 Canada*; E. HERBST and F. C. DE LUCIA, *Department of Physics, The Ohio State University, 174 W. 18th Ave., Columbus, OH 43210.*

The ground state spectrum of the three torsional sub-states (*trans*, *gauche+* and *gauche-*) of the asymmetric internal hydroxyl rotation in ethyl alcohol has been recorded through 652 GHz. Our previous *trans*^a and *gauche*^b work has been expanded to include approximately 3000 assigned transitions through J=40 and K_a=17 including approximately 1000 which show significant deviation from a standard asymmetric rotor pattern due to *trans-gauche* interactions. The location of these interactions has enabled us to determine the *trans-gauche* energy difference accurately. The application of a fixed-frame-axis method (FFAM) Hamiltonian to this asymmetric top-asymmetric frame internal rotation problem is discussed. The results of a three-state FFAM analysis are presented.

^aJ. C. Pearson, K. V. L. N. Sastry, M. Winnewisser, E. Herbst and F. C. De Lucia, *J. Phys. Chem. Ref. Data* **24**, 1 (1995).

^bJ. C. Pearson, K. V. L. N. Sastry, E. Herbst and F. C. De Lucia, *J. Mol. Spectrosc.*, in press (1996).

MF09

15 min 4:02

THE GROUND STATE TORSION-ROTATION SPECTRUM OF PROPARGYL ALCOHOL (HCCCH₂OH)

J. C. PEARSON, *Jet Propulsion Laboratory, California Institute of Technology, Mail Stop 183-301, 4800 Oak Grove Dr., Pasadena, CA 91109.*

The ground state torsion-rotation spectrum of the asymmetric internal hydroxyl rotation in propargyl alcohol (HCCCH₂OH) has been investigated in the 84 to 640 GHz range. The ground state has been confirmed to consist of two torsional sub-states of the *gauche* conformer^a, a symmetric *gauche* state (*gauche*+) and an antisymmetric *gauche* state (*gauche*-). No evidence of a low lying third state or *trans* conformer has been observed. The more stable *gauche*+ state is 652389.5 MHz below the *gauche*- state. Due to their close proximity, the two *gauche* states interact strongly through a series of *a*- and *b*-type Coriolis interactions. Strong *a*- and weak *b*-dipole rotational transitions are observed within each sub-state while strong *c*-dipole torsional transitions are observed between the two sub-states. Over 2300 transitions covering a range of *J* and *K_a* values to 80 and 34, respectively, have been fit to experimental accuracy using a fixed-frame-axis method (FFAM) Hamiltonian. The rotation, distortion and interaction constants have been determined. The 652 GHz *gauche*+–*gauche*- energy difference, strong *gauche*+ to *gauche*- transitions and the constants derived from the analysis should enable rapid astronomical detection.

^aEizi Hirota, *J. Mol. Spectrosc.* **26**, 335 (1968).

MF10

10 min 4:19

Microwave-Microwave Double-Resonance Assignment Of The *Gauche* Conformer Of Methyl Vinyl Ether

David A. McWhorter, Sam Cupp, Chung Yi Lee and Brooks H. Pate, *Department of Chemistry, University of Virginia, Charlottesville, VA 22901.*

An electric-resonance optothermal spectrometer has been used to perform microwave-microwave double-resonance measurements on the less stable conformer of methyl vinyl ether. The measured rotational constants are consistent with a *gauche* structure. The dipole moment components for this conformer have been measured using the Autler-Townes splitting of states that occurs in the presence of a strong, resonant microwave field. Rotational constants, dipole moments and the threefold barrier to internal rotation, *V*₃, will be reported. We have searched in double-resonance for the second tunneling component for the equivalent *gauche* conformer but have found no transitions. This suggests the tunneling gap is larger than about 2GHz.

MF11

15 min 4:31

MICROWAVE SPECTRA OF MOLECULES WITH MULTIPLE CONFORMATIONS: 2,2,4-TRIMETHYLPENTANE

A.R. Hight Walker, R.D. Suenram, G.T. Fraser, *Optical Technology Division, National Institute of Standards and Technology, Gaithersburg, MD 20899*; K.K. Irikura, *Chemical Kinetics and Thermodynamics Division, National Institute of Standards and Technology, Gaithersburg, MD 20899*.

The number of possible conformations in an organic molecule grows multiplicatively with the size of the C-C backbone. As the molecule of interest increases in chain length, it becomes more challenging experimentally and theoretically to determine the most favorable conformation. Moreover, as the number of possible conformations increases, the energy difference between the various conformers is expected to decrease, making it difficult to establish the ground-state conformer of the system. In the present work, we explore the problems of studying molecules which display a large number of potential conformations by examining the microwave spectrum of 2,2,4-trimethylpentane, the major component of gasoline. Semiempirical (AM1) and ab initio (HF/6-31G*) calculations are also undertaken on this system to help guide the experimental measurements and to explore the reliability of the theoretical methods for this relatively large molecule. Ignoring methyl-group rotations, the possible conformers differ by rotation about the C(2)-C(3) and C(3)-C(4) bonds. The theoretical calculations have identified three local conformational minima (A-C). The calculated relative energies for A, B, and C are 0, 250, and 1369 cm⁻¹, respectively, at the HF/6-31G* level. The barrier between the A and B conformers is calculated to be only 35 cm⁻¹. The molecular-beam Fourier-transform microwave spectrum of 2,2,4-trimethylpentane reveals a plethora of lines. At present, one set of *a*-type transitions have been assigned to one conformer of the molecule. The *a*-type transitions are split into doublets, separated by ~ 5 to 50 MHz, suggestive of a splitting due to tunneling. Efforts are presently underway to complete the assignment of the spectrum.

MF12

15 min 4:48

CHARACTERIZATION OF (Z)- AND (E)-ETHANETHIAL S-OXIDE BY PULSED-BEAM FT-MW SPECTROSCOPY, C. W. GILLIES, Department of Chemistry, Rensselaer Polytechnic Institute, Troy, NY 12180; J. Z. GILLIES, Department of Chemistry, Siena College, Loudonville, NY 12211; J.-U. GRABOW, Molecular Physics Division, National Institute of Standards and Technology, Gaithersburg, MD 20899.^a

(Z)- and (E)-Ethanethial S-oxide, geometrical isomers of CH₃CH=SO (methyl sulfoxide), were produced by pyrolyzing 2-methyl-2-propyl vinyl sulfoxide in a furnace maintained at 350 °C. A pulsed solenoid valve sampled the pyrolysis products in a Ne/He flow and the rotational spectra were obtained with a FT microwave spectrometer. Internal rotor splittings were observed for the (Z) form and a fit of the A-state normal isotopomer lines to a Watson Hamiltonian gave rotational constants of A = 14237.0861(5) MHz, B = 4678.4488(3) MHz and C = 3594.8008(2) MHz. A partial r_s structure of the (Z) isomer was determined from spectral assignments of a sulfur-34, two carbon-13 and two deuterium-substituted methyl group isotopomers. The spectral data show that one methyl hydrogen is located in the heavy atom plane oriented *syn* with respect to the oxygen. Electric dipole moment components of $\mu_a = 2.714(5)$ D and $\mu_b = 1.869(35)$ D were calculated from Stark shift measurements of the (Z) isomer. The (E) isomer did not exhibit internal rotor splittings and a fit of normal isotopomer *a*-type transitions to a Watson Hamiltonian gave A = 31128(27) MHz, B = 3475.8521(16) MHz and C = 3188.4429(23) MHz. An (E):(Z) ratio of 3:97 is estimated from a comparison of line intensities of the normal isotopomer of the (E) form with line intensities of the sulfur-34 isotopomer of the (Z) isomer.

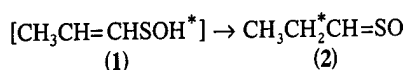
^aPresent address: Institut für Physikalische Chemie der Universität Kiel, D-24098 Kiel, Germany.

MF13

15 min 5:05

IN SITU DETECTION AND MECHANISM OF FORMATION OF THE ONION LACHRYMATOR, (Z)-PROPANETHIAL S-OXIDE, BY PULSED-BEAM FT-MW SPECTROSCOPY, J. Z. GILLIES, Department of Chemistry, Siena College, Loudonville, NY 12211; C. W. GILLIES, Department of Chemistry, Rensselaer Polytechnic Institute, Troy, NY 12180.

The pulsed-beam FT-MW technique utilizing a modified solenoid valve for continuous gas flow was adapted to detect the onion lachrymator (2) in the headspace above freshly prepared onion macerate. A monodeuterated isotopomer of (2), $\text{CH}_3\text{CHDCH}=\text{SO}$, was observed when the onion was processed with D_2O . Pyrolysis of 2-methyl-2-propyl 1'-propenyl sulfoxide with D_2O affords the same monodeuterated species, $\text{CH}_3\text{CHDCH}=\text{SO}$. Since (2) has no exchangeable hydrogens, these results provide strong support for mechanisms, both in the pyrolysis and the onion, which invoke a common intermediate, propenesulfenic acid, (1).^a The acidic hydrogen, H^* , on (1) exchanges with D_2O , leading to deuteration of (2) at the methylene hydrogen position,



H^* . Analogous results were obtained from the pyrolysis of 2-methyl-2-propyl vinyl sulfoxide with D_2O which produces $\text{CH}_2\text{DCH}=\text{SO}$. This pyrolysis provides evidence for reversibility in the above mechanism because $\text{CHD}_2\text{CH}=\text{SO}$ is found to be a minor product.

^aSee the recent review, E. Block, *Angew. Chem., Int. Edn. Engl.* **31**, 1135 (1992).

MF14

15 min 5:22

THE CONFORMATION AND INTERNAL ROTATION BARRIER IN BENZYL FLUORIDE

Robert K. Bohn, Sterling A. Sorenson, Nancy S. True, Thomas Brupbacher, Michael C. L. Gerry, and Wolfgang Jaeger

The rotational spectrum of benzyl fluoride is extremely dense when observed on a static gas sample with a Stark-modulated spectrometer. An unambiguous assignment was not found. Although the spectrum is considerably simplified in a pulsed-jet Fourier transform spectrometer, it is still remarkably rich and complex. Benzyl fluoride is nearly prolate ($\kappa = -0.86$) and the *a*-type transitions were easily identified and assigned. Many of the *a*-type transitions occur as unsymmetrical doublets with splittings of the order of tens of kHz and intensity ratios about 4/1. *c*-Type transitions also were identified, some of which show splittings up to 5 MHz. The spectrum has been accounted for with a model including a low barrier to internal rotation with an observable tunnelling splitting such that *a*-type selection rules allow transitions only between levels of the same symmetry, and *c*-type selection rules only between levels of different symmetry. Using different sets of parameters for the two species and a constant energy difference between their rotational energy levels, 150 transitions were fit to 10 kHz with an energy difference of 3.4 MHz between the two different symmetry species. We are continuing the analysis using a Hamiltonian which explicitly includes internal rotation of a C_{2v} top.

The observed value of P_{cc} , 16.89 amu-Å², and the fact that *c*-type and not *b*-type transitions are observed unambiguously define the conformation of benzyl fluoride as that with the plane containing the C-C-F chain orthogonal to the benzene ring.

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Address of Jaeger: Dept. of Chemistry, U. of Alberta, Edmonton, Alberta T6G 2G2

MG01**10 min 1:30****THE INFRARED SPECTRUM OF HBO**

P. Colarusso, K.-Q. Zhang, and P.F. Bernath, *Centre for Molecular Beams and Laser Chemistry, University of Waterloo, Waterloo, Ontario, Canada, N2L 3G1.*

The free radical HBO was generated in a high-temperature furnace at 1400°C. The infrared spectra of the two major isotopic species, H^{11}BO and H^{10}BO , were recorded in emission with a Fourier transform spectrometer (Bruker IFS 120HR). The wavenumber range from 400 to 3500 cm^{-1} was detected at a resolution of 0.01 cm^{-1} . The three fundamental vibrational bands as well as various combination and hot bands have been observed. A vibrational-rotational analysis of the spectra will be presented.

MG02**10 min 1:42****Infrared Spectroscopy of BrCNO**

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of Waterloo, Waterloo, Ontario, Canada, N2L 3G1.
T. Pasinszki, N. P. C. Westwood
Department of Chemistry and Biochemistry, University of Guelph, Guelph, Ontario,
Canada, N1G 2W1.

The transient molecule BrCNO was generated in situ by the pyrolysis of the Br_2CNOH precursor. The high resolution spectra of two vibrational bands of BrCNO were recorded and analyzed.

MG03**15 min 1:54**

INFRARED EMISSION SPECTRA OF MOLECULAR IONS IN FAST ION BEAMS, M.D. Tissandier, A. D. Earhart, and J.V. Coe, Department of Chemistry, The Ohio State University, Columbus, OH 43210-1173.

The feasibility of detecting and dispersing infrared emission spectra from collisionally activated fast ion beams has been demonstrated with a simple test apparatus. The apparatus and an initial low resolution spectrum will be presented. Progress regarding development into a simple, routine, and general method for recording low resolution infrared spectra of molecular ions in the hydrogen stretching region will be discussed.

MG04

15 min 2:11

EXCITATION TEMPERATURES DETERMINED FROM H_3^+ HOT BAND EMISSION IN THE JOVIAN IONOSPHERE

M.-F. JAGOD, and T. OKA, Department of Chemistry, Department of Astronomy and Astrophysics, and the Enrico Fermi Institute, The University of Chicago, Chicago, IL 60637-1403; T. R. GEBALLE, Joint Astronomy Centre, 660 N. A'ohōkū Place, University Park, Hilo, HI 96720

Since our observation of the $3.544 \mu\text{m } 2\nu_2^0 \rightarrow \nu_2 (J=9, K=9 \rightarrow J=8, G=9, U=1)$ hot band transition of H_3^+ in the polar regions of Jupiter,^a we have pursued the simultaneous detection of additional hot band transitions with fundamental band transitions in order to derive well determined H_3^+ excitation temperatures. We report 9 additional resolved $2\nu_2^0 \rightarrow \nu_2$ and $\nu_1 + \nu_2 \rightarrow \nu_1$ hot band transitions observed in emission at 3.52, 3.63, 3.66, and 3.84 μm . The hot band transitions have thus far only been detected in the polar regions, with the occasional exception being the 3.544 $\mu\text{m } 2\nu_2^0 \rightarrow \nu_2$ transition around 45° S latitude during the 1994 Comet Shoemaker Levy-9 encounter. Temporal and spatial variation of the excitation temperatures as well as their dependence on vibrational mode will be presented.

Anomalous line intensities, e.g. $R(3,3)^-$,^b will also be discussed.

All observations were made with the CGS4 spectrometer at the United Kingdom Infrared Telescope on Mauna Kea, Hawaii.

^aT. R. Geballe, M.-F. Jagod, and T. Oka, *Astrophys. J.* **408**, L109-L112 (1993).

^bJ.-P. Maillard, P. Drossart, J. K. G. Watson, S. J. Kim, J. Caldwell, *Astrophys. J.* **363**, L37-L41 (1990).

MG05

15 min 2:28

OBSERVATION OF A NONTHERMAL ORTHO-TO-PARA RATIO OF H_3^+ IN HYDROGEN PLASMAS: SPIN SELECTION RULES IN PLASMA CHEMISTRY

D. Uy, M. Cordonnier*, R.M. Dickson, K.E. Kerr, and T. Oka. Department of Chemistry and Department of Astronomy and Astrophysics, The University of Chicago, Chicago, IL 60637, *Laboratoire de Spectroscopie Hertzienne, Université des Sciences et Technologies de Lille, 59655 Villeneuve d'Ascq, France

Last year at this conference, we reported our observation of a nonthermal nuclear spin distribution of H_3^+ in hydrogen plasmas. Positive column and hollow cathode discharges with 100% parahydrogen as the source gas produced an H_3^+ ortho-to-para ratio of about 3:2 instead of the usual 1:1. Observing H_3^+ enriched in the para modification when para- H_2 is used proves that the nuclear memory is kept even after a chain of ion-neutral reactions. The selection rules based on permutation symmetry are the most robust ones in spectroscopy and collisional interactions and are not broken except in near degenerate cases.

The reaction $\text{H}_2 + \text{H}_2^+ \rightarrow \text{H}_3^+ + \text{H}$ will produce only para H_3^+ if both reactants are para¹, but a combination of ortho and para reactants would produce ortho and para H_3^+ . We have formulated a group theoretical method adapted from Quack's paper¹ to determine the branching ratios of chemical reactions according to the nuclear spin species of the reactants. The method is also applicable to subsequent hydrogen exchange reactions involving H_3^+ . Using steady-state rate equations in which the spin modification is explicitly stated, an H_3^+ ortho-to-para ratio was calculated which approximately explains the experimental value. The group theoretical method for determining spin modification branching ratios as well as the ion-neutral chemical kinetics will be presented.

¹Quack, M. *Mol. Phys.* **34**, 377, 1977.

MG06

15 min 2:45

OBSERVATION OF $\Delta |k-l|=3$ TRANSITIONS IN THE ν_3 BAND OF H_3O^+

D. Uy, E. White, and T. Oka. Department of Chemistry and Department of Astronomy and Astrophysics, The University of Chicago, Chicago, IL 60637.

Although the vibration-rotation spectrum of H_3O^+ has been studied extensively, there has been no experimental information on the value of the C rotational constant because of the absence of $\Delta |k-l| \neq 0$ forbidden transitions. There is a near degeneracy between the $(9,0)^+$ and the $(9,3)^-$ ground state rotation-inversion levels, as pointed out by Verhoeve, *et al.*¹ Indeed the ground state combination differences of the ν_3 fundamental transitions show a sizable shift of the $(9,3)^-$ level as well as the neighboring $(7,3)^-$ and $(11,3)^-$ levels. We have obtained 11 forbidden ν_3 transitions involving these ground state levels. This enabled us to determine the energy difference between different K levels and the mixing coefficient τ_{mix} . An extended analysis of the ν_3 bands is in progress.

¹Verhoeve, P., *et al.* *Chem. Phys. Lett.* **161**, 195, 1989.

MG07

15 min 3:02

Time-resolved Diode Laser Spectroscopy of the ν_3 Band of the Iron Dicarbonyl Radical $\text{Fe}(\text{CO})_2$

Keiichi Tanaka, Kouichi Sakaguchi, and Takehiko Tanaka

The ν_3 (CO antisym. stretch) fundamental band of $\text{Fe}(\text{CO})_2$ was observed by time-resolved infrared diode laser spectroscopy. The $\text{Fe}(\text{CO})_2$ radical was produced by 193 nm ArF excimer laser photolysis of iron pentacarbonyl $\text{Fe}(\text{CO})_5$. More than 50 lines in the 1924-1932 cm^{-1} region have been assigned to the ν_3 fundamental band of $\text{Fe}(\text{CO})_2$. Observed spectra are split into triplet, $\Omega = 0, 1^e$, and 1^f , due to spin-spin interaction. The spectral lines which have even N quantum number are missing due to the spin statistics of C ($I=0$) and O ($I=0$) nuclei. The observation indicates definitely that $\text{Fe}(\text{CO})_2$ is a linear molecule with $D_{\infty h}$ symmetry and the ground electronic state is $^3\Sigma^-_g$.

The rotational and centrifugal distortion constants determined are 1419.80(49) MHz and 4.73(37) kHz, respectively. The spin-spin interaction constant λ_0 determined is as large as 676 (56) GHz, which is comparable with that of FeCO (659 GHz) [1], but is much larger than that of $\text{Fe}(\text{CO})_3$ (12 GHz) [2]. The ν_3 band origin 1928.19023(52) cm^{-1} is lower than that of the ν_1 band of FeCO , 1946.4706 cm^{-1} [1].

[1] K. Sakaguchi, K. Tanaka, and T. Tanaka, to be published.

[2] Y. Kasai, Y. Ohshima, and Y. Endo, to be published.

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MG08

15 min 3:30

MID-INFRARED SPECTROSCOPY OF IONIC PROTON-BOUND COMPLEXES:
INTERMOLECULAR INTERACTION AND SOLVATION EFFECTS

OTTO DOPFER, SERGEY A. NIZKORODOV, MARKUS MEUWLY, JOHN P. MAIER, *Institut für Physikalische Chemie, Universität Basel, Klingelbergstrasse 80, CH-4056 Basel, Switzerland;*
EVAN J. BIESKE, *School of Chemistry, University of Melbourne, Parkville, Victoria 3052, Australia.*

Mid-infrared photofragmentation spectra of mass-selected proton-bound cluster ions of the type $B_n \dots H-A^+$ have been recorded, where A is either N_2 , CO, H_2O , NH_3 , or H_2 , while B are either rare gas atoms ($Rg = He, Ne, Ar$) or H_2 .

Rotationally-resolved spectra of the dimers ($n=1$) provide information about the intermolecular potential (equilibrium geometry, binding energy, effects of tunneling and internal rotation). For larger clusters ($n>1$), frequency shifts in vibrational spectra give rise to a consistent picture of cluster growth (microsolvation process). Recent results for $Ne_n \dots HCO^+$ ($n=1,2$) will be compared to those for the previously characterized $Ar_n \dots HCO^+$ series ($n=1-13$)^a.

^aS. A. Nizkorodov, O. Dopfer, T. Ruchti, M. Meuwly, J. P. Maier, and E. J. Bieske, *J. Phys. Chem.* 99, 17118 (1995)

MG09

15 min 3:47

Spin-Rotation and Hyperfine Spectroscopy in the Near-IR: A Study of the Methyl Radical, Scott Davis, David T. Anderson, and David J. Nesbitt

A glow discharge, slit supersonic expansion in conjunction with direct infrared laser absorption have been utilized to record high resolution vibration-rotation spectra of the CH_3 methyl radical. The slit supersonic expansion results in effective rotational cooling ($T_{rot} \leq 25$ K), collapsing the radical population into the lowest rotational levels for the two nuclear spin states ($I=3/2$ and $1/2$). All spectroscopically allowed vibration-rotation transitions from the lowest rotational level for each of the two nuclear spin states are observed and analyzed in the $v_3=1 \leftarrow 0$ vibrational manifold. Due to the high instrumental resolution (slit supersonic Doppler width ≈ 75 MHz), fully resolved spin-rotation splittings and partially resolved hyperfine splittings are observed. The magnitude of the hyperfine coupling constant probes the spin density at each hydrogen nucleus, and the negative sign of the Fermi contact parameter confirms the hydrogen nuclear spins are coupled to the unpaired radical via spin polarization across the CH bond.

Scott Davis: JILA, National Institute of Standards and Technology and Department of Chemistry and Biochemistry, University of Colorado, Boulder, Colorado 80309-0440.

MG10**15 min 4:04****High Resolution Infrared Absorption Spectroscopy of Jet-Cooled Molecular Ions, Scott Davis, David T. Anderson, and David J. Nesbitt**

A slit-jet discharge nozzle has been constructed to investigate jet-cooled molecular ions with direct absorption infrared spectroscopy. As a first test of the discharge source rovibrational spectra of two protonated ions, H_2O^+ and HN_2^+ , generated in a pulsed slit-jet expansion have been studied using a narrow band (2 MHz) IR difference frequency laser in the $3\ \mu\text{m}$ region. Extensive cooling of the nascent molecular ions is produced by the supersonic expansion as demonstrated by a 25 K rotational Boltzmann plot for HN_2^+ in a Ne expansion. The low temperature and "collision free" environment provided by the supersonic expansion has two desired effects: (i) it serves to stabilize the gas-phase molecular ions and (ii) it increases the sensitivity of the technique by significantly narrowing the transition lineshape. Work is currently aimed at exploiting the dynamics of ion formation at very low temperatures to study small molecular ions and molecular ion clusters; the most recent results will be presented.

Scott Davis: JILA, National Institute of Standards and Technology and Department of Chemistry and Biochemistry, University of Colorado, Boulder, Colorado 80309-0440.

MG11**15 min 4:21****Observation of ν_4 band transitions of NH_4^+ and ND_4^+**

Changhong Xia, Maria M. Sanz and Stephen C. Foster, *Department of Chemistry, Mississippi State University Mississippi State, MS 39762-9573.*

The tetrahedral ammonium ion has two triply-degenerate infrared-active fundamentals. In 1983, Crofton and Oka; and Schafer, Begemann, Gudeman and Saykally observed the ν_3 fundamental of NH_4^+ in glow discharges. Several subsequent studies have been reported, but only one concerns the other IR-active fundamental. In this work, more than thirty new lines in the ν_4 band of NH_4^+ are reported, together with the first detection of the same band of ND_4^+ .

These ammonium ions were observed in a water-cooled hollow cathode discharge with a diode laser spectrometer. A program was written to fit the spectra to fourth order based upon the spherical top Hamiltonian of Robiette *et al.* and using an uncoupled basis set.

MG12**15 min 4:38****The ground-state of protonated carbonyl sulfide, HOCS^+ or OCSH^+ ?**

Maria M. Sanz, Changhong Xia, Stephen C. Foster and Svein Saebo, *Department of Chemistry, Mississippi State University Mississippi State, MS 39762-9573.*

Ab initio calculation by Scarlett and Taylor predicted that S-protonated OCS is more stable than the O-protonated isomer. Experimental evidence appears to contradict this finding. Nakanaga and Amano observed a band of protonated OCS at $3435\ \text{cm}^{-1}$ and assigned it to the O-H stretching vibration. Although they also searched near $2500\ \text{cm}^{-1}$, they didn't observe any spectrum which could be attributed to an S-protonated isomer.

We have carried out *ab initio* calculation at the MP2/6-311G++(2df,2pd) and QCISD levels and have confirmed the conclusions of Scarlett and Taylor. The S-protonated form is predicted to be more than 4 kcal/mol more stable than the O-protonated isomer. This calculation and the results of our experimental search for the S-protonated will be reported.

MG13**15 min 4:55**

DIODE LASER TRANSIENT ABSORPTION SPECTRUM OF THE ETHYL RADICAL, TREVOR J. SEARS, PEI JIN, Department of Chemistry, Brookhaven National Laboratory, Upton, NY 11973-5000, PHILIP M. JOHNSON, Department of Chemistry, State University of New York, Stony Brook, NY 11974 and SUSAN OATIS, Department of Chemistry, Long Island University, Southampton, NY 11968.

The CH_2 rocking fundamental of the ethyl radical, C_2H_5 , has been observed at wavelengths close to 18.9 microns. The spectrum shows evidence for a very low barrier to internal rotation, or torsion, and exhibits complex torsion-rotation structure. It has been analysed using a model Hamiltonian based upon a molecular reference structure of G_{12} symmetry. A preliminary analysis of the spectrum has recently been published,^a and we report here on subsequent progress. We have employed a slightly refined Hamiltonian and identified several series of R-branch transitions in the 540-550 cm^{-1} region. They are thought to derive from levels belonging to non-degenerate symmetry species. Such levels contain the most easily accessible information on the size of the torsional potential in the spectrum and confirmed assignments should enable an improved determination of the torsional potential as well as structural parameters.

Acknowledgement: Work at Brookhaven National Laboratory was carried out under Contract No. DE-AC02-76CH00016 with the U. S. Department of Energy and supported by its Division of Chemical Sciences, Office of Basic Energy Sciences.

^a T. J. Sears, P. M. Johnson, P. Jin and S. Oatis, J. Chem. Phys. **104**, 781 (1996).

MG14**5 min 5:12**

INFRARED DIODE LASER SPECTROSCOPY OF THE $\text{X}^2\Pi$ CCl RADICAL, PEI JIN, BOR-CHEN CHANG, AND TREVOR J. SEARS, Department of Chemistry, Brookhaven National Laboratory, Upton, New York 11973-5000.

The infrared spectrum of carbon chloride (CCl) in the 11.8 μm region was obtained at Doppler-limited resolution following ArF excimer laser photolysis of HCClBr_2 . Previous investigations^{a,b} have observed mostly $\text{X}^2\Pi$ vibrational fundamental transitions with J up to 30. However, due to the limited J values, some fine structure parameters, such as the Λ -doubling parameters, p , and q_v , could not be well determined. In the present study, we have observed J up to 50 and, in addition, a few hot band (2,1) transitions were also observed. The more extensive data should lead to better determined molecular parameters for $\text{X}^2\Pi$ CCl .

Acknowledgment: This work was carried out under Contract No. DE-AC02-76CH00016 with the U.S. Department of Energy and supported by its Division of Chemical Sciences, Office of Basic Energy Sciences.

^aC. Yamada, K. Nagai, and E. Hirota, J. Mol. Spectrosc. **85**, 416 (1981).

^bJ. B. Burkholder, A. Sinha, P. D. Hammer, and C. J. Howard, J. Mol. Spectrosc. **127**, 61 (1988).

MG15

15 min 5:19

Concentration modulation technique for a continuous-scan FTIR spectrometer

Takashi Imajo, Shinobu Inui, Keiichi Tanaka, and Takehiko Tanaka, *Department of Chemistry, Faculty of Science, Kyushu University 33, Hakozaki, Higashi ku, Fukuoka 812-81, Japan.*

A new concentration modulation technique for a FTIR spectrometer was devised, and applied to the measurement of infrared emission spectra of OH X $^2\Pi$ ($v = 1 \rightarrow 0$) to demonstrate the selectivity in detection of short-lived species in discharge plasmas. Compared to the modulation technique developed by Guelachvili's group¹, in which the FTIR spectrometer is operated in the step-scan mode, the present technique may generally be used with commercially available FTIR instruments operating in the continuous-scan mode. A similar technique with high frequency (50 kHz) polarization modulation has already been reported², although the modulation frequency must be in the 10 kHz range or higher. The present technique is operative at low (~ 1 kHz) modulation frequencies.

The principle of the present method is as follows. The output signal of the IR detector is doubly modulated by ac discharge and by optical pass difference of the scanning interferometer. The doubly modulated signal is first demodulated by a PSD at the discharge frequency (2 kHz). The PSD is modified so that an output time constant circuit is replaced by a narrow band pass filter. The center frequency ω of the filter is set at the frequency where, without concentration modulation, the IR emission to be observed would give interferogram. The interferogram with frequencies near ω selected by the band pass filter is fed to the A/D converter of the IFS120HR spectrometer. The rest of the data processing is the same as in the case of an ordinary pass difference modulation spectrum. The infrared emission signal of OH X $^2\Pi$ ($v = 1 \rightarrow 0$) was observed with maximum intensity when the reference sine wave was in-phase with the discharge, and disappeared when out of phase.

1. A. Benidar, G. Guelachvili, and P. A. Martin, *Chem. Phys. Lett.*, **177**, 563 (1991).
2. L. A. Nafie, M. Diem, and D. W. Vidrine, *J. Am. Chem. Soc.*, **101**, 496 (1979).

MG16

10 min 5:36

High Resolution FTIR Spectroscopy of the PO Radical

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The high resolution (0.0035cm^{-1}) spectrum of PO for the fundamental band in the ground electronic state ($^2\Pi_r$) was observed using IFS120HR Fourier transform spectrometer with a White-type discharge absorption cell. The effective optical length was 16 m. The PO radical was generated in a AC discharge (20kHz, 300mA) plasma of $\text{POCl}_3(40\text{ mTorr}) + \text{Ar}(500\text{ mTorr})$. In total of 196 signals were assigned to the P- and R-branch lines of both $\Omega = \frac{1}{2}$ and $\frac{3}{2}$ substates. The Λ -type doubling of the $^2\Pi_{\frac{1}{2}}$ state was well resolved both for P and R branches. Molecular constants of the $v=1$ excited vibrational state are accurately determined, and the precision of the rotational constant and centrifugal distortion constant are improved by about one order in comparison with the result of diode laser spectroscopy⁽¹⁾. Molecular constants of the ground vibrational state are also precisely determined by using the combination difference method together with the microwave data⁽²⁾.

1. J. Butler, K. Kawaguchi, and E. Hirota *J. Mol. Spectrosc.* **101**, 161 (1983).
2. K. Kawaguchi, S. Saito, and E. Hirota *J. Chem. Phys.* **79**(2), 629 (1983).

MH01**15 min 1:30**

LINE MIXING SUM RULES FOR QUASIELASTIC COLLISIONS IN MULTIPLY SPECTRA, A.S. PINE, Optical Technology Division, National Institute of Standards and Technology, Gaithersburg, MD 20899.

In the impact approximation, the spectra of transitions overlapped by collisional broadening is given by a sum over Lorentzian absorption and dispersion profiles about each transition. The dispersion components arise from the interference among lines coupled by the collisions, and their magnitude and sign is given by the line mixing coefficient. When the transitions have identical dipole moments and originate from nearly degenerate energy levels, as often occur in doublet or multiplet spectra, the collisions are quasielastic and the line mixing coefficients sum to zero. Additionally, the sum of the broadening coefficients, the integrated intensities and the shifts are conserved, although these parameters and the line mixing coefficients may be transferred among the multiplet components nonlinearly with pressure. Some illustrative examples of coupled doublets and A, E and F symmetry multiplets in the J manifolds of a spherical top (eg. CH₄) will be presented along with a prescription for incorporating Doppler broadening and Dicke narrowing in experimental spectra.

MH02**15 min 1:47**

N₂ AND Ar BROADENING AND LINE MIXING IN THE P AND R BRANCHES OF THE ν_3 BAND OF METHANE, A.S. PINE, Optical Technology Division, National Institute of Standards and Technology, Gaithersburg, MD 20899.

N₂- and Ar-broadened spectra of the allowed P- and R-branch manifolds for $J \leq 10$ in the ν_3 band of CH₄ have been recorded from the Doppler limit to ~ 67 kPa at $T = 295$ K using a tunable difference-frequency laser spectrometer. As noted in our previous study¹ of the Q branch of ν_3 , the transition-dependent broadening coefficients are very similar for the different buffer gases, as are the P and Q branches, with the R branch exhibiting somewhat larger variations. Line intensities, pressure shifts and Dicke narrowing coefficients are also obtained. Strong line mixing among the blended tetrahedral components is observed, similar to that reported by Benner and coworkers^{2,3} using FTIR measurements. An analysis is presented restricting line coupling among transitions of the same nuclear spin A, E or F symmetry with the sum of the mixing coefficients for a given symmetry in the J manifold constrained to zero.

1. A.S. Pine, J. Chem. Phys. **97**, 773 (1992).

2. D.C. Benner, V.M. Devi, M.A.H. Smith and C.P. Rinsland, JQSRT **50**, 65 (1993).

3. D.C. Benner, C.P. Rinsland, V.M. Devi, M.A.H. Smith and D. Atkins, JQSRT **53**, 705 (1995).

MH03

15 min 2:04

M-RESOLVED COLLISION-INDUCED ROTATIONAL ENERGY / ALIGNMENT TRANSFER
IN CH₄STEPHEN L. COY, JODY J. KLAASSEN, and JEFFREY I. STEINFELD, MIT Chemistry, 77 Mass.
Ave, Cambridge, MA 02139 (Coy and Steinfeld), JILA, Boulder, CO (Klaassen)

Experiments vary widely in their sensitivity to molecular space-fixed orientation. Fluorescence, absorption, raman, double resonance, and other techniques each have distinct dependencies on the M quantum number, and reactive collisions depend on relative orientations. The specific behavior of M on collision leaves its traces on the lineshapes and amplitudes in each type of experiment. Descriptive and rigorous angular momentum scaling tools like the statistical-tensor and tensor-opacity expansion provide a framework for understanding experimental observables and for modeling collisional interactions.

It is quite common that state-to-state rates observed in 4-level DR experiments account for only about 70% of the linewidth seen in direct absorption. We relate this discrepancy to M-resolved collision-induced rotational energy/alignment transfer as part of the interpretation of results of 3 and 4 level DR experiments on ground-state E spin-modification levels in methane.

MH04

15 min 2:21

Pressure shifts in the ν_3 -band of NO₂ induced by collisions with noble gases, N₂, H₂, D₂, O₂, CO₂, and SO₂

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Very high resolution (0.0005 cm⁻¹) infrared spectra of NO₂ have been recorded with a pulse driven diode laser spectrometer. The 1600 cm⁻¹ region corresponding to the ν_3 -band has been analysed. 34 lines ($6 \leq N'' \leq 38$, $0 \leq K'' \leq 11$), with NO₂ pressure varying from 0.1 to 0.5 Torr and foreign gas (Xe, Kr, Ar,...) from 100 to 220 Torr were recorded, using a Herriot cell of 4.7 m pathlength due the weakness of lines. The results clearly shows (within experimental accuracy) a notable variation of shift with respect to N'' quantum number, the shifts being larger in negativ magnitude for big N'' . One can also note that the values of shifts are not systematically lower for molecules with higher broadening coefficients as it is for H₂O^a. The similarities and differences between H₂O and NO₂ will be discussed.

*B.S. acknowledges a grant from the *Deutsche Forschungsgemeinschaft*

^aB.Grossmann and E.Browell, *J.Mol. Spectrosc.* **138**, 562 (1989)

MH05

15 min 2:38

Self- and Foreign Gas Broadening in the $\nu_1 + \nu_3$ Band of SO_2^*

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Experimental results concerning the self-broadening of about 100 lines in the $\nu_1 + \nu_3$ band of SO_2 near 2499 cm^{-1} will be presented. The experiments were carried out with a tunable diode laser spectrometer in pulsed mode. The dependence of the broadening coefficient on the rotational quantum number J'' and K_a'' will be presented together with the comparison to our former results concerning the ν_1 and ν_3 band, respectively. In the studied quantum number range $2 \leq J'' \leq 47$, $0 \leq K_a'' \leq 13$ we observe similar to the other bands a pronounced K_a'' dependence but only a weak J'' dependence. The investigations are completed by measurements with the perturbers He, Ne, Ar, Kr, Xe, N_2 , O_2 , H_2 , and D_2 for some selected lines.

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*** V.V.L. acknowledges a grant from the *Deutscher Akademischer Austauschdienst*

MH06

15 min 2:55

Temperature and Quantum Number Dependence of Broadening Coefficients in the ν_3 Band of SO_2

B. SUMPF*, M. SCHNE, H.-D. KRONFELDT, *Optisches Institut der Technischen Universität Berlin, Sekr. PN 0-1, Hardenbergstr. 36, 10623 Berlin, Germany*.

Systematic investigations concerning the dependence of the self-broadening coefficient $\gamma_{\text{SO}_2-\text{SO}_2}$ on the quantum number J'' and K_a'' are presented for 23 lines with $8 \leq J'' \leq 33$ and $1 \leq K_a'' \leq 16$ at room temperature applying a diode laser spectrometer. We found that $\gamma_{\text{SO}_2-\text{SO}_2}$ shows a typical decrease with increasing K_a'' whereas the J'' dependence is not typical as in the case of the ν_1 band. For the same lines collisions with air and hydrogen were studied. As in the case of self-broadening we found a similar behavior in the quantum number dependence. To complete our studies we measured the temperature dependence of the line broadening coefficients in the range between 250K and 360K with the perturbers air, helium, neon, argon, krypton, and xenon. For three lines with $J'' = 8$ and $K_a'' = 1, 2, 3$ the noble gas broadening was studied whereas seven lines with $8 \leq J'' \leq 30$ and $1 \leq K_a'' \leq 9$ were measured in the case of air broadening. The temperature coefficient n ranges between 0.56 and 0.89 for the noble gases and between 0.72 and 0.99 for air. For the noble gases one can suppose a weak decrease of n with rising atomic weight of the perturber although the experimental uncertainties are relatively large due to the restricted temperature range.

* B.S. acknowledges a grant from the *Deutsche Forschungsgemeinschaft*

MH07

15 min 3:12

INFRARED ABSORPTION CROSS-SECTIONS AND BAND STRENGTHS OF HFC-32 VAPOUR (DIFLUOROMETHANE)

G DUXBURY AND K SMITH, *Department of Physics and Applied Physics, Strathclyde University, Glasgow G4 0NG, Scotland, UK*; D NEWNHAN, M PAGE AND JOHN BALLARD, *Atmospheric science division, Space science Department, Rutherford Appleton Laborator, Chilton, Didcot, OX11 0QX, UK.*

Recent legislation controlling the use of Chlorofluorocarbons (CFCs) has led to the introduction of replacement compounds, hydrochlorofluorocarbons (HCFCs), in a wide range of domestic and industrial applications. However, from 2030 the usage of HCFCs will also be controlled and the more environmentally acceptable Hydrofluorocarbons (HFCs) will probably replace them.

The C-H bonds present in HCFCs and HFCs allows destruction in the atmosphere by reaction with OH radicals, significantly reducing the lifetime of these compounds compared with CFCs. However, many HCFC and HFC compounds absorb strongly in the mid-infrared, particularly in the 8-12 μm "atmospheric transmission window" region. It is therefore important to include data on these absorptions in the radiative transfer calculations used to model warming of the Earth's atmosphere.

Medium resolution (0.03 cm^{-1}) Fourier Transform Infrared Spectroscopy was used to determine absorbance cross-sections and integrated band strengths of the ro-vibrational absorption bands of HFC-32 lying in the region 600 to 1900 cm^{-1} . Measurements were performed at eight temperatures (203, 212, 222, 243, 253, 264, 287 and 297 K) for pure vapour samples, and at three temperatures (203, 253 and 297 K) for mixtures containing 5, 20 and 100 kPa of dry air.

The derived absorbance cross-sections have been submitted for inclusion in the AFGL HITRAN database, and are available via the anonymous FTP site at The University of Strathclyde (kashmir.phys.strath.ac.uk).

Intermission

MH08

15 min 3:45

HITEMP — HIGH-TEMPERATURE MOLECULAR ABSORPTION DATABASE FOR H₂O, CO₂ AND CO

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RICHARD B. WATTSON, *Stewart Radiance Laboratory, Utah State University, Bedford, MA 01730*;
ROBERT R. GAMACHE, *Center for Atmospheric Research, Univ. of Mass. Lowell, Lowell, MA 01854*; and
JOHN SCHROEDER, *Ontar Corp., 9 Village Way, N.Andover MA 01845-2000*

The latest version of the HITRAN/HAWKS database has recently been released. The HITRAN database has been recognized for more than 20 years as the international standard compilation of spectroscopic absorption parameters for atmospheric gases. Significant new additions have been made to the database to keep pace with the increasing requirements of the user community. One of these additions is a high-temperature database (HITEMP) for H₂O, CO₂, and CO at temperatures in excess of 1000K. These data will be of particular importance in high-temperature molecular spectroscopy, remote sensing of high-temperature sources such as flames, combustion processes, exhaust plumes, and stellar atmospheres. This paper will describe the latest additions to HITRAN, the high-temperature database, and present calculations showing the difference between the HITEMP and HITRAN databases for high temperature sources. Comparisons will be made with other calculated databases and laboratory data.

This effort has been supported by the Air Force Office of Scientific Research and the US Department of Energy.

MH09

15 min 4:02

VIBRATIONAL ENERGIES AND ROTATIONAL CONSTANTS OF $^{12}\text{C}^{16}\text{O}_2$

D. CHRIS BENNER, V. MALATHY DEVI, *Department of Physics, College of William and Mary, Williamsburg, VA 23187-8795*; CURTIS P. RINSLAND and MARY ANN H. SMITH, *Atmospheric Sciences Division, NASA Langley Research Center, Mail Stop 401A, Hampton, VA 23681-0001*.

The positions of about 5000 spectral lines of $^{12}\text{C}^{16}\text{O}_2$ have been accurately measured with a multispectrum nonlinear least squares fitting technique^a. The spectra were obtained with the Fourier Transform Spectrometer at the McMath-Pierce facility of the National Solar Observatory at Kitt Peak at a resolution of 0.01 cm^{-1} with a natural carbon dioxide sample. These positions are from the 1830 to 4000 cm^{-1} spectral region and include about 100 vibration-rotation bands. The wavenumber scales of the spectra were carefully calibrated to the same standard, making the data set homogeneous. There are approximately 60 vibrational levels represented by the bands and over 50 of them are tied together by combinations of observed bands. All of the vibrational energies and rotational constants for these bands have been determined in one global solution. The individual positions were weighted according to the uncertainties of the positions as determined by the spectrum fits. For each band at least one of the vibrational levels is constrained by most or all of the other bands. As a result, this produces values superior to those from single band solutions. The uncertainties in the differences of the various combinations of parameters are also readily available using the derived uncertainties in the parameters and the correlations between parameters.

^aD. Chris Benner, C. P. Rinsland, V. Malathy Devi, M. A. H. Smith and D. Atkins, *JQSRT* **53**, 705-721 (1995).

MH10

10 min 4:19

ABSOLUTE INTENSITIES OF CO_2 LINES IN THE 1830 TO 4000 cm^{-1} SPECTRAL REGION

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Absolute intensities for over 10,000 transitions belonging to approximately 200 vibration-rotation bands of eight isotopic species of carbon dioxide in the spectral region between 1830 and 4000 cm^{-1} have been measured using a multispectrum nonlinear least-squares fitting technique^a. A total of 6 spectra of a high-purity (99.995% minimum) natural sample of CO_2 recorded at 0.01-cm^{-1} resolution using the Fourier transform spectrometer at the McMath-Pierce facility of the National Solar Observatory at Kitt Peak were used for the analysis. These data were obtained at room temperature with sample pressures and pathlengths varying from 1 to 10 Torr and 25 to 386 m respectively. A few new bands which have not been predicted so far were identified and their intensities were determined. In addition, intensities of several pairs of interacting bands in $^{12}\text{C}^{16}\text{O}_2$ and $^{13}\text{C}^{16}\text{O}_2$ were also measured. The intensities obtained for each band have been analyzed to determine the vibrational intensity and nonrigid rotor coefficients. Comparisons between the results obtained in this study and other published values will be presented.

^aD. Chris Benner, C. P. Rinsland, V. Malathy Devi, M. A. H. Smith and D. Atkins, *JQSRT* **53**, 705-721 (1995).

MH11

15 min 4:31

COMPARISON OF CO₂ ABSOLUTE INTENSITIES FOR BANDS NEAR 4000 cm⁻¹

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Our two groups have been measuring absolute intensities of CO₂ lines in different spectral regions. One group (William and Mary/NASA Langley) has measured bands from 1830 to 4000 cm⁻¹ and the other (NASA Ames/JPL) from 4000 to 8000 cm⁻¹. These two datasets contain three bands in common near the limits of each group's data.

For this comparison both groups used room temperature spectra of pure natural carbon dioxide obtained using the Fourier transform spectrometer at the McMath-Pierce facility of the National Solar Observatory to measure the intensities of the $2\nu_3-\nu_2$ and $\nu_2+2\nu_3-2\nu_2^2$ bands of ¹²C¹⁶O₂ and the $2\nu_1+2\nu_2^0$ band of ¹⁶O¹²C¹⁸O. The two sets of data were analyzed independently. The three William and Mary/NASA Langley spectra (386 meter path, 1 to 10 Torr pressure) were analyzed with a multispectrum nonlinear least squares fitting technique then the derived line intensities fitted by nonlinear least squares to the full equation for line intensity. The six NASA Ames/JPL spectra (49 to 410 meter path length, 45 to 80 Torr pressure) were analyzed with a single spectrum nonlinear least squares fitting technique, the results of the spectra suitably averaged, then the resulting data reduced to a dipole moment. The resulting dipole moments were least squares fitted to a polynomial whose coefficients are the Herman-Wallis factors. The predicted line intensities of the strongest band ($2\nu_3-\nu_2$) generally agree within 3%. Linear and cubic Herman-Wallis coefficients were found to be significantly different than zero. The band strengths agree to only 9%. This discrepancy is attributed to the high correlation between the linear Herman-Wallis coefficient and the band strength in the solution.

A comparison of these results with values obtained by each group analyzing the data of the other group as well as the results from an analysis of the combined data sets will also be presented.

MH12

15 min 4:48

THE HOT BANDS OF METHANE BETWEEN 5 AND 10 MICRONS

O. Ouadi, J. C. Hilico, M. Loete, *Laboratoire de Physique de l'Université de Bourgogne*; and L. R. Brown, *Jet Propulsion Laboratory, California Institute of Technology, 4800 Oak Grove Drive, Pasadena, California 91109*.

The experimental line intensities of 1727 transitions between 1000 and 2000 cm⁻¹ belonging to the pentad-dyad system of methane are fitted to first and second order using the effective dipole moment expansion in the polyad scheme. The nine observed bands are $\nu_3-\nu_2$, $\nu_3-\nu_4$, $\nu_1-\nu_2$, $\nu_1-\nu_4$, $2\nu_4-\nu_4$, $2\nu_2-\nu_4$, $2\nu_2-\nu_2$, $\nu_2+\nu_4-\nu_2$ and $\nu_2+\nu_4-\nu_4$. The intensities are obtained from long-path spectra recorded at 0.005 cm⁻¹ resolution using the McMath Fourier transform spectrometer located at Kitt Peak National Observatory. To achieve a more stable fit for three of the 27 constants required in the second order model, 1206 intensities of the dyad (ν_2 , ν_4) are refitted simultaneously with the hot band data. The fits to first and second order lead to rms values, respectively, of 21.5% and 5.0% for the 1727 hot band intensities and 6.5% and 3.0% for the 1206 dyad lines. The band strengths of all 10 pentad-dyad hot bands range from 0.93 for $2\nu_4-\nu_4$ to 7.7×10^{-5} for the unobserved $2\nu_4-\nu_2$ in units of cm⁻²/atm at 296 K.

Part of the research reported in this paper was performed at the Jet Propulsion Laboratory, California Institute of Technology, under contract with the National Aeronautics and Space Administration.

MH13

15 min 5:05

SELF-BROADENING COEFFICIENTS FROM FTIR MEASUREMENTS OF H₂O

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Self-broadening parameters have been extracted for selected transitions in the ν_1 , $2\nu_2$ and ν_3 bands of water vapor observed between 2500–4200 cm⁻¹. The H₂O spectrum at room temperature in natural isotopic abundance has been recorded in this region at pressure-broadening-limited resolution with a Bruker FTS 120HR and a White-type cell adjusted to provide pathlengths of 64.5–288.5m. Sample pressures used were 0.007–29.7mbar (0.005–22.3 Torr). Broadening coefficients determined for transitions in the ν_2 band of water vapor in this study and earlier works^a are comparable. The results of the broadening determinations are presented and discussed.

^aJ. -Y. Mandin, C. Camy-Peyret, and J. -M. Flaud, *J. Quant. Spectrosc. Radiat. Transfer* **26**(6), 483–494 (1981).

MH14

15 min 5:22

MEASUREMENTS OF O₃ LINE INTENSITIES IN THE ν_3 BAND

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To obtain a more comprehensive data set for determination of absolute intensities of ozone lines in the 9–11 μ m region, we have recorded additional high-resolution absorption spectra of ozone at room temperature using the Fourier transform spectrometer at the McMath-Pierce facility of the National Solar Observatory at Kitt Peak. As in our previous effort,^a the spectrometer was set up in double-pass mode^b to cover the 800–1400 cm⁻¹ region at 0.0027 cm⁻¹ resolution. The ozone samples were contained in a glass cell having crossed IR-transmitting and UV-transmitting paths approximately 10 cm in each direction. A 254 nm UV-absorption monitor of the same design as Pickett et al.^c was used to measure the ozone partial pressures, which were kept at approximately 0.3 to 0.5 Torr to prevent the appearance of saturated lines in any region of the band. Four spectra, for which the ozone partial pressure varied by < 1.0 percent during the recording time, were selected for analysis. Using our multispectrum nonlinear least-squares procedure,^d we have fit these spectra simultaneously to determine intensities for numerous lines in both the *P* and *R* branches of the ν_3 fundamental band. These results will be compared with other recent measurements^{e,f} and with the values on the 1992 HITRAN compilation.

^aM. A. H. Smith, V. Malathy Devi, D. Chris Benner, and C. P. Rinsland, 50th International Symposium on Molecular Spectroscopy, Paper RG02 (1995).

^bD. E. Jennings, R. Hubbard, and J. W. Brault, *Appl. Opt.* **24**, 3438 (1985).

^cH. M. Pickett, D. B. Peterson, and J. S. Margolis, *J. Geophys. Res.* **97**, 20,787–20,793 (1992).

^dD. Chris Benner, C. P. Rinsland, V. Malathy Devi, M. A. H. Smith, and D. Atkins, *JQSRT* **53**, 705–721 (1995).

^eM. R. DeBacker and D. Courtois, 50th International Symposium on Molecular Spectroscopy, Paper RA06 (1995).

^fM. R. DeBacker, B. Parvitte, V. Zeninari, and D. Courtois, *JQSRT* **54**, 1009–1018 (1995).

MH15**10 min 5:39****INVESTIGATION OF THE WATER VAPOR LINESHIFTS IN THE (010)-(000) AND (011)-(000) BANDS**

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Water vapor lineshifts induced by nitrogen pressure have been measured at NIST (USA) and LPMA (France) using Fourier-spectrometers with a multi-pass absorption cells of 32 and 84 meters at 0.0025 and 0.01 cm^{-1} resolution in 1850 – 2230 cm^{-1} and 4900 – 5600 cm^{-1} spectral region. The special procedure have been used to minimize errors connected with the assymetry of the contours due to apparatus effects in high pressure FTS-spectra.

The fitting of Voigt contour parameters was used to obtain lineshift parameters. Accuracy of lineshift coefficient determination was better than 1 mk/atm. The lineshift coefficients have been determined for well resolved isolated lines belonging to 010-000 and 011-000 bands with high quantum numbers J up to 18.

The lineshift coefficients have been calculated using the Anderson method and cut-of-free procedure. The dipole-quadrupole, quadrupole-quadrupole, dipole-hexadecapole and polarizational interactions were included in the calculations.

The contributions of different type of intermolecular potentials and their dependences on J value will be discussed.

MH16**15 min 5:51****SYNCHRONOUSLY SCANNED OPO CARS: A NEW TOOL FOR MOLECULAR SPECTROSCOPY**

PETER C. CHEN, *Spelman College, 350 Spelman Ln. Box 307, Atlanta, Georgia, 30314*.

Results are presented from the development of a new nonlinear spectroscopic method for molecular vibrational spectroscopy. This method uses the Optical Parametric Oscillator (OPO) and synchronous scanning to overcome problems that have limited the scan range for nonlinear Raman spectroscopy in the past. This new improvement transforms nonlinear Raman spectroscopy into a more appealing tool for studying molecular species.

TA01**30 min 8:30****NEW ASPECTS OF THE INTRACAVITY LASER ABSORPTION SPECTROSCOPY**

F. STOECKEL, *Laboratoire de Spectrométrie Physique Université J. Fourier/CNRS/Grenoble BP87 38402 Saint Martin d'Hères Cedex France.*

Intracavity laser absorption spectroscopy (ICLAS) is now a well established direct multiplex absorption method with a high sensitivity. This phenomena was discovered about 25 years ago [?, ?]. ICLAS is based on the high sensitivity of a broadband laser to intracavity frequency dependent losses: broadband intracavity losses are compensated by the laser gain whereas for narrow lines, the laser operates like a multipass cell without reflection losses. Equivalent absorption path lengths of several hundred of kilometers may be reached.

Since the discovery of this effect, ICLAS has been used with success for the spectroscopy of very weak transitions mainly with dye, color center or Nd:glass lasers [?]. The new class of solid state laser is highly promising for the development of a new type of highly sensitive spectrometer in the infrared or near infrared[?].

We will give an overview about the principle of this technique and about recent applications like spectroscopy with an intracavity supersonic jet, with high resolution... We also will examine the possibilities to use this powerful technique for measurements of weak concentrations of trace gas with an all solid state ICLAS spectrometer for in-situ detection.

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TA02**15 min 9:05****INTRACAVITY LASER ABSORPTION SPECTROSCOPY AS A LABORATORY TECHNIQUE: STATE OF THE ART**

A. KACHANOV, *Laboratoire de Spectrométrie Physique Université J. Fourier/CNRS/Grenoble BP87 38402 Saint Martin d'Hères Cedex France.*

Intracavity laser absorption spectroscopy (ICLAS) regardless that it is one of the most sensitive among high resolution spectroscopic methods, is still far from being widely used. One of the reasons is that the commercial equipment for ICLAS is not yet available, so there exists a common opinion that one who wants to install and use ICLAS in the laboratory needs a very high degree of laser technical expertise.

The goal of this talk is, in contrast to this opinion, to outline rather simple general requirements to ICLAS components, and to demonstrate examples of the most advanced setups, which have been used during last years in several groups. It will be clear that, as a matter of fact, the ICLAS setup is significantly simpler than for example narrowband tunable lasers. The experimental procedure from filling the intracavity cell with a sample gas to obtaining several hundreds wavenumbers of calibrated spectrum will be described in details. The limitations of the method, the most favorable areas of application, the sensitivity limits, which could be achieved in the usual laboratory practice as well as promising future developments of ICLAS will be discussed. The talk is intended to provide some useful guidelines to those who wish to start using this technique.

TA03

15 min 9:22

SENSITIVITY LIMITS OF INTRACAVITY ABSORPTION SPECTROSCOPY

V.M. BAEV, J. SIERKS, T. LATZ, R. BOEHM, J. HUENKEMEIER, P.E. TOSCHEK, *Institut fuer Laser-Physik, Universitaet Hamburg, D-20355 Hamburg, Germany.*

Emission spectra of multimode lasers are very sensitive to selective absorption in the cavity. The sensitivity of measurements grows with the laser pulse duration t . The absorption signal in the laser spectrum is equivalent to the signal obtained by the conventional absorption technique, when the length of the absorption cell is replaced by the velocity of light times t . The ultimate sensitivity obtained with a cw laser is limited by quantum noise, at a small pump rate, and by nonlinear mode coupling at high pump rate. The optimum pump power and the highest sensitivity to absorption are individual features of the actual laser. Reliable identification of the dominant type of nonlinear mode coupling allows one to optimize the laser parameters for the highest sensitivity. Up to now, the highest spectral sensitivity has been obtained with a cw Rh6G dye laser. The nonlinear mode coupling in this laser is determined by four-wave mixing on the saturated laser gain, and by stimulated Brillouin or Rayleigh scattering. Reduction of these interactions by increasing the cavity length to 3 m, and by decreasing the cavity loss to about 2% per round trip, have resulted in spectral sensitivity to absorption which is equivalent to 70.000 km absorption length, at the pump rate being 1% above the laser threshold. Further enhancement of the sensitivity is possible in a strongly dispersive cavity. A Ti:sapphire laser shows stronger limitation of sensitivity due to four-wave mixing, since the gain medium is 100 times longer. The spectral sensitivity reached with this laser is equivalent to 1000 km absorption path length. Rare-earth-doped fiber lasers exhibit strong second-order nonlinearity due to their small cross section and comparatively long fibers. The sensitivity to absorption achieved now with these lasers corresponds to 100 km of absorption path. The emission spectrum of diode lasers is determined mostly by quantum noise due to extremely high loss in their cavities. The equivalent absorption length, achieved with this type of laser is about 10 km. Identification of particular factors that limit the sensitivity in each of these lasers allows one to optimize the laser parameters for most precise, sensitive, and reliable measurements.

TA04

10 min 9:39

ABSORPTION COEFFICIENTS AND BAND STRENGTHS FOR THE 703 NM AND 727 NM BANDS OF METHANE AT 77 K

James J. O'Brien and Kuldip Singh, Department of Chemistry and Center for Molecular Electronics, University of Missouri-St. Louis, St. Louis, MO 63121-4499.

The technique of intracavity laser spectroscopy has been used to obtain methane absorption spectra for the vibrational overtone bands that occur around 703 nm and 727 nm. Absorption coefficients for the 690-742 nm range have been obtained for a sample temperature of 77 K at a spectral resolution of $<0.02 \text{ cm}^{-1}$. A new method of data analysis is utilized in obtaining the results. It involves deconvolving the many ILS spectral profiles that comprise the absorption bands and summing the results. Values averaged over 1 cm^{-1} and 1 \AA intervals are provided. Band strengths also are obtained. The total intensities of the 703 and 727 nm bands are in reasonable agreement with previous laboratory determinations which were obtained for relatively high pressures of methane at room temperature using lower spectral resolution. The methane bands appear in the reflected sunlight spectra from the outer planets. Results averaged over 1 nm intervals are compared with other laboratory studies and with those derived from observations of the outer planets. The band profiles differ considerably from other laboratory results but are in good accord with the planetary observations. Laboratory spectra of methane at appropriate conditions are required for the proper interpretation of the observational data. Absorption spectra can provide some of the most sensitive diagnostic data on the atmospheres of those bodies.

ACKNOWLEDGEMENTS

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TA05

10 min 9:51

INTRACAVITY LASER SPECTROSCOPY AT ULTRA-HIGH RESOLUTION - QUANTITATIVE DETERMINATION OF LINE STRENGTHS USING A NEW METHOD FOR DATA ACQUISITION

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A new method of acquiring intracavity laser absorption spectra (ILS) has been developed that enables spectra to be obtained at much higher spectral resolution than has been possible previously.¹ Using the usual method for acquiring ILS spectra, the resolution obtained is determined by the resolving power of the associated spectrograph. Even with multi-pass, echelle grating spectrographs, the maximum resolution reported in practice is about 800,000. The new technique enables considerably better resolution to be achieved. It involves use of an intracavity etalon and the observation that the intensity of an etalon fringe is reduced if the fringe occurs in vicinity of an absorption feature. In addition, the position of the etalon fringe does not change. The fringe positions can be determined very accurately. The etalon is tuned across its free spectral range and the absorption spectrum recovered by summing the series of intracavity etalon spectral profiles. The intensities of several water lines occurring around 720 nm were examined using the new approach. A standing wave dye laser was employed and the etalon was tuned using a high resolution stepping motor. Results obtained over a series of water pressures show the applicability of the Beer-Lambert relationship for ILS. This study demonstrates that quantitative data at very high sensitivity and ultra-high resolution can be obtained using the new approach.

1. A. Kachanov, F. Stoeckel, A. Charvat, and J.J. O'Brien; to be published.

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TA06

15 min 10:03

INTRACAVITY LASER ABSORPTION SPECTROSCOPY OF FLAMES. HCO RADICAL DETECTION IN METHANE/AIR FLAME

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Formyl radical, HCO, was monitored for the first time in an atmospheric pressure premixed hydrocarbon flame. Intracavity Laser Absorption Spectroscopy (ICLAS) based on quasi-cw argon-ion pumped dye laser was used. HCO absolute concentration profile was also measured in 30 torr flat methane/air flame. The ability of ICLAS to the absolute concentration and temperature measurements in flames is discussed. The sensitivity of the detection is $1 \cdot 10^{12} \text{ cm}^{-3}$ and can be improved with isolation of the laser cavity from atmospheric water background.

TA07

10 min 10:20

TIME RESOLVED ICLAS SPECTROSCOPY of HO₂ RADICAL

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HO₂ radical absorption spectrum was recorded in the 1.22-1.27 μm range with the spectral resolution 0.13 cm^{-1} using intracavity laser absorption spectrometer based on F_2 color centers LiF laser. The rotationally resolved vibronic bands: (0,0,0)-(0,0,0), (0,2,0)-(0,1,0) and (0,0,2)-(0,0,1) of the $A' - A''$ electronic transition were analyzed. The mechanism of the forbidden rotational subbands appearance will be discussed.

Intermission

TA08

10 min 10:45

INTRACAVITY LASER SPECTROSCOPY

N. A. RASPOPOV, E. A. SVIRIDENKOV, and S. E. VINOGRADOV ^a, *Lebedev Physical Institute, Leninsky pr. 53, Moscow, 117924 Russia.*

Intracavity laser spectroscopy (ICLS) with the broadband lasers is one of the most sensitive techniques of the absorption spectral analysis. The ICLS sensitivity is fundamentally limited by laser spontaneous emission. This allows one to detect frequency-dependent losses of the order of average cavity losses divided by the number of photons in single mode. For CW broadband lasers, this quantity equals to $3 \cdot 10^{-12} \text{ cm}^{-1}$, which corresponds to the optical path of $3 \cdot 10^{11} \text{ cm}$. On the other hand, the ordinary dye laser sensitivity is limited by approximately 10^{-9} cm^{-1} , which corresponds to the effective time of "spectral memory" of a few milliseconds. We believe that this is determined by nonlinear mode interaction in the laser active media. Nonlinear interaction leads to energy transfer from more intensive modes to the neighboring modes whose intensity is reduced by the absorption. This results in the smearing of the dips in the laser emission spectrum. We performed the experimental and theoretical study of the nonlinear mode dynamics of the multimode broadband CW dye laser determined by the stimulated Brillouin scattering and the four-wave parametric mixing. The regimes of stochastic generation, dynamic chaos and regular self-oscillations have been observed. It is shown, that the influence of nonlinear interactions can be minimized by employing a unidirectional ring laser with compensated cavity dispersion. In such lasers, the stable kinetics of generation was achieved up to times of 100 milliseconds even in the case of nonselective cavity. It provides the sensitivity as high as 10^{-11} cm^{-1} and allows one to detect the absorption of a few atoms per cubic centimeter.

^aSupport by Soros International Science Foundation research grant and Russian Foundation for Basic Research grant is gratefully acknowledged

TA09

15 min 10:57

ULTRASENSITIVE DUAL-BEAM ABSORPTION SPECTROSCOPY, BASED ON WAVELENGTH-MODULATION TECHNIQUE AND LOGARITHMIC NOISE CANCELING

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Various registration methods for ultrasensitive diode laser based absorption spectroscopy are discussed. The sensitivity of a single-beam wavelength modulation technique is limited by excess laser noises and wavelength-dependent effects in optical system. A dual-beam logarithmic detection allows to reduce excess laser noises but actually shot-noise level is not usually achieved and sensitivity is limited by low-frequency transmittance fluctuations and a flicker noise from atomizer. Simultaneous using a double-beam logarithmic detection and a wavelength-modulation technique allows to minimize a low-frequency noise contribution. Absorbance of $7 \times 10^{-8} / (\text{Hz})^{-1/2}$ in such a system is demonstrated. Applications to trace measurements of chlorine in glow-discharge atomizer and lithium in graphite tube atomizer are described.

TA10

15 min 11:14

INTRACAVITY ABSORPTION VERSUS RING-DOWN, RELATIVE PERFORMANCE

D. ROMANINI, A. KACHANOV, *Laboratoire de Spectrométrie Physique Université J. Fourier/CNRS/Grenoble BP87 38402 Saint Martin d'Hères Cedex France.*

Cavity ring-down spectroscopy (CRDS) and intra-cavity laser absorption spectroscopy (ICLAS) are the direct absorption methods most performant in terms of sensitivity ($\sim 10^{-10} \text{ cm}^{-1}$) and spectral capabilities. In CRDS, the losses of an optical cavity are monitored by observing the exponential decay (ring-down) of light injected into the cavity by a narrow-band laser pulse. The sample is placed inside the cavity and its absorption spectrum is given by the variations in the ring-down rate as the laser is tuned. The spectral resolution is practically limited by the laser, while the spectral extent that can be covered in a single experiment is limited by the working range of the mirrors composing the optical cavity, which is typically more than 50 nm in the visible. In CRDS the broad-band losses of the cavity should be less than about 1% per pass, a fact that constitutes a serious limitation in many practical applications.

In ICLAS, the sample is placed directly into the cavity of a laser operating broad-band. Then, broad-band cavity losses are compensated by the laser gain, so that samples having broad-band losses of more than 1% can be studied without the degradation of the sensitivity. Here, the sample absorption lines are detected as dips in the wide laser emission spectrum. They increase according to the Lambert-Beer law over a pathlength equal to ct_g , where t_g is the time since when the laser is started (generation time) and c is the speed of light.

A major limitation of ICLAS is that one can detect only spectral features sufficiently narrower than the laser emission profile, which is typically less than 10 nm wide at $t_g \sim 100 \mu\text{s}$ ($ct_g \sim 30 \text{ km}$). Things become gradually worse when pushing to higher sensitivity, since the laser emission spectrum narrows as the square root of t_g . On the other hand, since the emission spectrum is recorded as a whole, this technique has the definite advantage of an intrinsic multiplexing capability.

In conclusion, CRDS and ICLAS are somewhat complementary methods with respect to the fields of possible practical application. Current perspectives of technical improvement, partly based on the availability of new solid-state and semiconductor lasers, lead us to believe that in the near future it will be possible to build very compact and portable devices based on CRDS and ICLAS. These devices would cover the spectral range from the near infrared to the near UV with a sensitivity which theoretically could be as high as 10^{-12} cm^{-1} for both techniques.

TA11

10 min 11:31

QUANTITATIVE ABSORPTION PARAMETERS FOR LINES IN THE 790 NM BAND OF WATER OBTAINED USING INTRACAVITY LASER SPECTROSCOPY WITH A Ti:SAPPHIRE LASER

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The intracavity laser spectroscopy (ILS) technique has been shown to be a very sensitive method for observing absorption spectra. By considering quantitative results (line strengths and pressure-broadening coefficients) obtained using the ILS method with a dye laser, we have demonstrated that the technique provides quantitative information that is in excellent agreement with that afforded by more traditional methods for acquiring absorption spectra.¹ A similar investigation has been conducted for an ILS system based on a Ti:sapphire laser. Presented are quantitative results for water vapor transitions occurring around 790 nm. Line intensities are determined as a function of water vapor pressure and effective pathlength (i.e., generation time). The line strengths are compared with values determined using the Fourier transform spectrometer at the Kitt Peak National Observatory.² The good agreement between these results demonstrates that quantitatively accurate data can be obtained using the intracavity technique with Ti:sapphire lasers.

1. K. Singh and J.J. O'Brien, *J. Mol. Spectrosc.* **167**, 99 (1994).
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TA12

10 min 11:43

INTERCAVITY LASER ABSORPTION SPECTROMETER BASED ON YAG: CR⁴⁺ LASER FOR 1340 – 1680 nm SPECTRAL REGION

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An intercavity laser absorption spectrometer was constructed on the basis of the full solid state continues wave YAG:Cr⁴⁺ laser. In addition to first work ^a the investigation of linearity and sensitivity of such spectrometer was performed. Dimensions of z-scheme laser setup were optimized to obtain the maximal absorption sensitivity. It was shown that the spectrometer can operate with an equivalent optical path more than 300 km. The sensitivity equal to 10⁻⁹cm⁻¹ was reached.

^aD. A. Gilmore, P. Vujukovic Gvijin and G. H. Atkinson, *Opt. Commun.*, 103(1993), 370.

TA13

10 min 11:55

MEASUREMENTS OF GROUND STATE OXYGEN, WATER VAPOR AND TEMPERATURE IN CHEMICAL OXYGEN-IODINE LASER BY TI:SAPPHIRE LASER-BASED INTRACAVITY LASER SPECTROSCOPY

M. P. FROLOV, Yu. P. PODMARKOV ^a, *Lebedev Physical Institute, Leninsky pr. 53, Moscow, 117924 Russia*.

The ground state oxygen and water vapor are important species in chemical oxygen-iodine laser. The detectivity required in the chemical oxygen-iodine laser device is about 0.03 Torr for both H₂O and O₂(X). We have shown that these parameters and the temperature of chemical oxygen-iodine laser medium can be measured by intracavity laser spectroscopy based on simple standing wave Ti:sapphire laser. Using 120-μs laser generation time, we have demonstrated the detection sensitivities to be 6 · 10¹⁴ and 3 · 10¹⁴ cm⁻³ for H₂O and O₂(X), respectively. The oxygen concentration measurement error does not exceed 5% in the range 2 · 10¹⁵–10¹⁶ cm⁻³. The temperature measurement error does not exceed 25K in the range 200-500K.

^aSupport by Russian Foundation for Basic Research grant is gratefully acknowledged

TB01**15 min 8:30****VIBRATIONAL ACTIVITY IN THE S_1 - S_0 SPECTROSCOPY OF PARA, META, AND ORTHOFLUOROTOLUENES**

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In support of IVR studies involving internal rotation in these fluorotoluenes, we have extended the cold jet S_1 - S_0 fluorescence excitation (FE) and single vibronic level fluorescence (SVLF) spectroscopy from the benchmark work of Okuyama, Mikami and Ito^a. The goal is to characterize the dominant vibrational activity. P-difluorobenzene (pDFB) has been used for comparison. A close correspondence occurs between pDFB and pFT. The main structure in both the zero point level SVLF spectrum and the FE spectrum is assigned with activity in the same three modes. If one does not look too closely, the molecules are twins. Two of these modes also contribute to the dominant vibrational structure in mFT and oFT. Additional dominant activity is also apparent in these molecules, but it comes from only two other modes even though the reduced symmetry allows about two-thirds of the modes to be totally symmetric. Thus the principal S_1 - S_0 vibrational activity in these fluorotoluenes have more similarities than differences. On the other hand, an abundance of low intensity vibrational structure makes mFT and oFT spectra appear qualitatively different from those of pFT and pDFB.

^aK. Okuyama, N. Mikami and M. Ito, *J. Phys. Chem.* **89**, 5617 (1985).

TB02**15 min 8:47****INTERACTION BETWEEN VIBRATIONS AND INTERNAL ROTATION IN S_1 M-FLUOROTOLUENE AS SEEN IN THE S_1 - S_0 SPECTROSCOPY**

QUAN JU, AND CHARLES S. PARMENTER, *Department of Chemistry, Indiana University, Bloomington, IN 47405*.

In support of IVR studies in m-fluorotoluene, a detailed picture is being constructed of the vibrational and internal rotation level structure for the lower 430 cm^{-1} of the S_1 state. Particular emphasis is given to Fermi resonances involving interactions between internal rotation and vibration. The information is derived from cold jet S_1 - S_0 spectroscopy with abundant use of dispersed single vibronic level fluorescence (SVLF). Seventy-five levels involving internal rotation as well as eight modes occurring as fundamentals, overtones and combinations occur with known zero order identities in the energy region. Of these, twenty-six have been pumped for examination by SVLF spectroscopy. Clear evidence for numerous level interactions appears in the spectra. The details are now being worked out.

TB03**15 min 9:04****Electronic Spectroscopy Of Hydrocinnamic Acid**

J.A.Dickinson, P.W.Joireman, R.W.Randall, E.G.Robertson, J.P.Simons, *Physical and Theoretical Chemistry Laboratory, Oxford University, South Parks Road, Oxford*.

We present one and two color resonant two-photon ionization (R2PI) spectra for hydrocinnamic acid (HCA) and its van der Waals complexes with water, $\text{HCA}-(\text{H}_2\text{O})_n$, where $n = 1 - 5$. Different conformations in the alkyl side chain produce two spectral bands in the 0_0^0 region. Conformation specific solvation effects are observed in the spectra of the $\text{HCA}-(\text{water})_n$ vdW complexes. Rotational band contours (resolution $\sim 0.08 \text{ cm}^{-1}$), have been obtained for the two conformer origin bands of HCA and the water complexes associated with these origins up to $n = 2$ water molecules. Band contours indicate that the water molecules do not significantly alter the polarization characteristics of the band. The results are interpreted in terms of reasonable structures for the monomers and van der Waals complexes.

TB04**15 min 9:21****SPECTROSCOPY OF SOME N-PHENYL AMIDES. STRUCTURES AND RELATIVE STABILITIES OF THE *CIS* AND *TRANS* ISOMERS**

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Equilibrium geometries and isomer distributions in a series of N-phenyl amides were studied using multiphoton ionization spectroscopy in a supersonic jet. The experimental data are consistent with a considerably larger population of the *trans* isomer in formanilide, although both isomers were present in the expansion. In the *cis* conformation the phenyl ring is twisted out of the plane of the amide group, while *trans*-formanilide adopts a planar geometry. Only *trans*-acetanilide was identified under the same experimental conditions. N-methyl substitution in formanilide results in different *cis* to *trans* isomer ratios, with a preference for the *cis* geometry. In addition, van der Waals clusters of formanilide and acetanilide with water were investigated and evidence of multiple binding sites was seen.

TB05**15 min 9:38****EVIDENCE FOR S_1/S_2 ELECTRONIC STATE MIXING IN THE $S_1 \rightarrow S_0$ FLUORESCENCE EXCITATION SPECTRUM OF 1-NAPHTHOL.* SUSAN HUMPHREY AND DAVID W. PRATT**

The role of S_1/S_2 state mixing in the $S_1 \rightarrow S_0$ spectrum of naphthalene is well known. The 8_0^1 vibronic band, coupled to the S_2 state, is polarized along the short molecular axis, unlike the 0_0^0 band which is polarized along the long axis. We have observed similar behavior in the $S_1 \rightarrow S_0$ electronic spectrum of 1-naphthol. Analysis of the rotationally resolved spectrum of the vibronic band at $\Delta E = 414 \text{ cm}^{-1}$ of *trans*-1-naphthol reveals that the transition dipole is tilted towards the short axis. Additionally, the spectrum is perturbed. These effects are attributed to coupling of this vibrational level in the S_1 state to the S_2 state which may influence the proton transfer behavior of 1-naphthol.

*Work supported by NSF (CHE9224398).

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TB06**15 min 9:55** **$S_1 \rightarrow S_0$ TRANSITION MOMENT ORIENTATIONS IN AROMATIC ETHERS,* JASON W. RIBBLETT AND DAVID W. PRATT**

Rotationally resolved fluorescence excitation spectra of the four origin bands that appear in the $S_1 \rightarrow S_0$ electronic transition of methyl-3-methoxybenzoate have been obtained and analyzed. The four origins have been assigned to conformers associated with the *cis* and *trans* configurations of the OCH_3 substituent and *cis* and *trans* configurations of the ester substituent, based on their inertial parameters. Further analysis makes possible the determination of the absolute orientation of the transition moment in the molecular frame of each of the four conformers and its dependence upon both the inertial and electronic properties of the substituents.

*Work supported by NSF.

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TB07

15 min 10:30

RYDBERG TRANSITIONS ORIGINATING AT METAL-LOCALIZED ORBITALS IN LARGE POLYATOMIC MOLECULES: A GAS-PHASE SPECTROSCOPIC STUDY OF TRANSITION- METAL SANDWICH COMPLEXES

S. Yu. KETKOV, *G.A. Razuvayev Institute of Organometallic Chemistry of Russian Academy of Sciences, Nizhny Novgorod 603600, Russia.*

The transition-metal sandwich compounds with an occupied totally symmetric valence molecular orbital (MO) derived from the metal d_{z^2} appear to represent the first example of polyatomic molecules revealing in the photoabsorption spectra well-resolved Rydberg transitions from a metal-localized MO. The gas-phase UV absorption spectra of $(\eta^6\text{-Arene})_2\text{M}$ ($\text{M} = \text{V}, \text{Cr}, \text{Mo}, \text{W}$), $(\eta^5\text{-C}_5\text{H}_5)_2\text{M}$ ($\text{M} = \text{V}, \text{Fe}, \text{Ru}, \text{Os}$), $(\eta^6\text{-Arene})(\eta^5\text{-C}_5\text{H}_5)\text{Mn}$, $(\eta^7\text{-C}_7\text{H}_7)(\eta^5\text{-C}_5\text{H}_5)\text{M}$ ($\text{M} = \text{V}, \text{Nb}, \text{Cr}, \text{Mo}, \text{W}$) show sharp bands arising from the transitions originating at the metal d_{z^2} orbital and terminating at Rydberg ns, np and nd levels. Due to the low d_{z^2} ionization energies, even higher Rydberg excitations in these compounds lie, as a rule, below 50000 cm^{-1} making it easy to investigate them using standard UV-visible spectrometers. Rydberg features disappear on going to the condensed media resulting in a dramatic difference between the gas-phase and solution-phase spectra of sandwich complexes. All Rydberg bands observed have been assigned on the basis of corresponding term values and effective quantum numbers. These parameters appear to change very little on going from one sandwich to another. For bisarene and mixed sandwiches, many-membered Rydberg np series converging on the d_{z^2} ionization limit have been revealed and the corresponding ionization potentials have been calculated with high accuracy using the Rydberg formula. Clear examples of molecular symmetry influence on the Rydberg structure, Rydberg/valence mixing and vibronic coupling in Rydberg states will be presented.

TB08

15 min 10:47

HUND'S CASE (a) -CASE (b) TRANSITION IN THE SINGLET-TRIPLET SPECTRUM OF PYRAZINE IN A SUPERONIC JET,* EMILE S. MEDVEDEV AND DAVID W. PRATT

We report theoretical calculations of the $T_1\text{-}S_0$ excitation spectrum of pyrazine, pyrazine- d_4 , and the pyrazine-Ar van der Waals complex. Towards this end, a closed analytical formula for the intensities of individual rovibronic transitions has been derived. The triplet state Hamiltonian includes, in addition to the usual rigid rotor terms, both intramanifold spin-spin coupling and intermanifold spin-orbit coupling. Taking reasonable values for these parameters leads to several experimental predictions, including a transition from Hund's Case (a) to Case (b) with increasing J and the appearance of fine structure splittings at even moderate spectral resolution. Detailed examples will be discussed.

*Work supported by the U.S. NAS/NRC CAST Program, by the U.S. National Science Foundation (CHE-9224398), by the International Science Foundation (SDQ000, NJ6000, NJ6300), and by the Russian Foundation for Basic Research (95-03-08130a).

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TB09

10 min 11:04

Rotationally resolved Coherent Ion Dip Spectroscopy of high lying ground state van der Waals vibrations of the benzene · Ar complex

R. Neuhauser, J. Braun, and H.J. Neusser, *Institut für Physikalische und Theoretische Chemie, Technische Universität München, Lichtenbergstr. 4, D-85748 Garching, Germany.*

Optical-optical double resonance experiments with intense, nearly Fourier transform limited nanosecond laser pulses are performed to investigate the electronic ground state (S_0) potential surface of benzene · Ar. To combine very high resolution and high sensitivity we apply the recently developed method of *Coherent Ion Dip Spectroscopy (CIS)*^{a, b} that is based on coherent light-matter interaction. The *CIS* method makes use of the special population dynamics in few level systems, interacting with two intense Fourier transform limited ns-laser pulses in special time sequences. Using a pulse sequence different from that of recent STIRAP population transfer experiments^c we showed that a nearly 100% blocking of ionization is possible for double resonance conditions in aromatic molecules and molecular clusters. This leads to 100% deep ion dips. New results for the S_0 ground state of the benzene·Ar complex are presented. Here, the high resolution of the *Coherent Ion Dip Spectroscopy* method allows the determination of very small isotope shifts of the van der Waals frequencies while the high sensitivity leads to the detection of hitherto not observed higher quanta of the van der Waals vibrations. In this way independent experimental data can be obtained to test theoretical calculations on mode mixing effects in the van der Waals potential without introducing additional free parameters into the calculations.

The isotope shifts for various van der Waals vibrations are compared to recent theoretical quantum mechanical 3D calculations of this model system performed by van der Avoird et al.

^aR. Neuhauser, R. Sußmann, and H.J. Neusser, *Phys. Rev. Lett.* 74, 3141 (1995)

^bR. Sußmann, R. Neuhauser, and H.J. Neusser, *J. Chem. Phys.* 103, 3315 (1995)

^cS. Schiemann, A. Kuhn, S. Steuerwald, K. Bergmann, *Phys. Rev. Lett.* 71, 3637 (1993)

TB10

15 min 11:16

Rotationally resolved high ($n > 100$) Rydberg states in a polyatomic molecule

R. Neuhauser, K. Siglow, and H.J. Neusser, *Institut für Physikalische und Theoretische Chemie, Technische Universität München, Lichtenbergstr. 4, D-85748 Garching, Germany.*

High electronic valence states and low Rydberg states ($n < 5$) in molecules display very short lifetimes due to fast nonradiative relaxation processes. Typical time constants in these energy regions are found to be in the sub-picosecond range.

At very high excitation energies, close to the ionization continuum, however, electronic states resembling the Rydberg states of hydrogen are expected. They consist of electronic states with a single electron excited into a quasi classical orbit around the positively charged molecular core with high Rydberg quantum number n . These Rydberg states are long-lived due to their weaker interaction with the molecular core. In polyatomic molecules the energetic separation of neighbored high n Rydberg states with Energy E_n (s. eq.(?)) becomes comparable or smaller than the spacing of vibrational or even rotational levels of the molecular core.

(In eq. (??) $R_{benzene}$ denotes the mass corrected Rydberg constant, $\mu(l)$ the quantum defect that is dependent on the angular momentum quantum number l of the electron, IE ionization energy and E_n the energy of the n^{th} Rydberg state)

$$E_n = IE - \frac{R_{Benzene}}{(n - \mu(l))^2} \quad (1)$$

Using sub-Doppler double resonance excitation combined with pulsed field ionization techniques we were able to resolve *individual* high n Rydberg states in this interesting energetic region in a polyatomic molecule for the first time. It is shown that for a selected J_K intermediate rovibrational state in benzene, C_6D_6 , several Rydberg series up to $n > 100$ with nearly vanishing quantum defect are observed converging to different limits. The intensity of these series in the pulsed field ionization experiments depends strongly on applied electric fields in the range from 20 to 200 mV/cm. The pulsed field ionization signal has a "decay time" in the microsecond range which is longer than expected from extrapolations of measured lifetimes of low Rydberg states of benzene and is ascribed to l -mixing in the applied electric fields.

TB11

15 min 11:33

Jet Spectroscopy of the $D_1\ 2^2B_1 - D_0\ 1^2B_1$ Electronic Transition of the *p*-Cyanobenzyl Radical

Masaru Fukushima, *Advanced Technology Research Center, Mitsubishi Heavy Industries, LTD., Sachiura, Kanazawa, Yokohama 236, Japan*; Kinichi Obi, *Department of Chemistry, Tokyo Institute of Technology, Ohokayama, Meguro, Tokyo 152, Japan*.

We have generated the *p*-cyanobenzyl radical in supersonic free expansion, and measured the laser induced fluorescence (LIF) spectra in green-blue region; the vibrationally and rotationally resolved LIF excitation spectra and the LIF dispersed spectra from the single vibronic levels (SVL). On the basis of the vibronic structures in the SVL dispersed spectra, the lowest energy band at 20735 cm^{-1} with the strongest intensity in the excitation spectrum has been assigned to the 0_0^0 band of the visible spectrum. Based on the band type of the 0_0^0 band, *a*-type, determined from the rotationally resolved LIF excitation spectrum, we have definitely assigned the visible band to the $D_1\ 2^2B_1 - D_0\ 1^2B_1$ electronic transition. We have found on the grounds of the vibrational analysis of the dispersed spectra, that the vibronic structure of the $2^2B_1 - 1^2B_1$ electronic transition of the benzyl type was characterized by totally symmetric fundamental modes, $1, 8a$, and $9a$, with the frequencies higher than 800 cm^{-1} , while those of the $1^2A_2 - 1^2B_1$ electronic transition are non-totally symmetric modes, $6b$ and $8b$, and totally symmetric modes, $6a$ and 1 , with the frequencies lower than 800 cm^{-1} ^a.

^aM. Fukushima, K. Obi, *Chem. Phys. Lett.* **248**, 269 (1996)

TB12

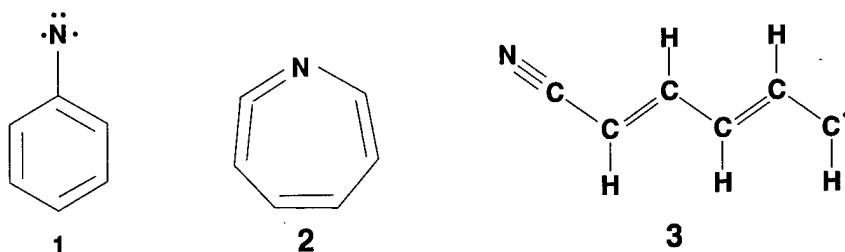
15 min 11:50

TOWARDS THE LIF SPECTRUM OF PHENYLNITRENE: YET ANOTHER PRECURSOR THAT YIELDS SOMETHING ELSE

MICHAEL B. PUSHKARSKY, DAVID E. POWERS, CHRISTOPHER C. CARTER, JAMES M. WILLIAMSON, TIMOTHY A. BARCKHOLTZ AND TERRY A. MILLER, *Laser Spectroscopy Facility, Department of Chemistry, The Ohio State University, Columbus, Ohio 43210*.

The excimer photolysis of $\text{C}_6\text{H}_5\text{-N=S=O}$ was expected to lead to scission of the N-S bond to yield triplet SO and triplet phenyl nitrene, **1**. We observed SO following KrF excimer photolysis of the precursor in a free jet expansion by probing its $\tilde{B}\ ^3\Sigma^- \leftrightarrow \tilde{X}\ ^3\Sigma^-$ transition. A rich LIF spectrum beginning at $19,500\text{ cm}^{-1}$ and extending beyond $20,500\text{ cm}^{-1}$ was also observed. The origin of the spectrum and two additional bands have been rotationally resolved. The rotational constants of 0.945 GHz (B) and 0.943 GHz (C) are irreconcilable with the carrier of the spectrum being phenyl nitrene. Rotational constants for the deuterated molecule have also been obtained and support this argument.

To aid in the identification of the photoproduct, we have performed *ab initio* calculations on phenyl nitrene and several other possible molecules that have been observed in solution and matrix studies of phenylnitrene (see figures, below). Of the calculated rotational constants and vibrational frequencies, only those for the carbene **3** are consistent with the experimental data.



TC01

15 min 8:30

ROTATIONALLY INDUCED STABLE QUANTUM MECHANICAL STATES,

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Poznań, Poland; J. Konarski

A new form of potential describing the interaction between atoms at a long distances will be presented.

Introduction of the interaction of induced dipole moment with an electric charge into an effective potential describing either intermolecular or intercomplex interaction leads to quantum mechanical states whose stability depends on rotational quantum number J .

Forms of the potential and its eigenvalues will be discussed during the presentation.

TC02

15 min 8:47

The potential energy surface of H_2^{16}O

Oleg L. Polyansky, *Department of Physics and Astronomy, University College London, Gower Street, London WC1E 6BT, UK*; Per Jensen, *FB 9-Theoretische Chemie, Bergische Universität-Gesamthochschule Wuppertal, D-42097 Wuppertal, Germany*; Jonathan Tennyson, *Department of Physics and Astronomy, University College London, Gower Street, London WC1E 6BT, UK*.

We report here a new determination of the H_2^{16}O potential energy surface from experimental data. The calculations have been carried out by means of the very accurate and highly efficient method proposed and applied to H_2^{16}O in a recent paper^a. This previous work has been significantly improved by inclusion of additional terms in the analytical expression used to represent the potential energy surface. Previously, 1600 rotation-vibration term values for H_2^{16}O were fitted with a standard deviation of 0.36 cm^{-1} . With the extended model of the present work, this standard deviation could be improved to 0.25 cm^{-1} . With the extended model and the new fitted potential function we have calculated a data set comprising 3200 term values, all of which can be compared with experimentally derived values. The standard deviation for this data set is 0.6 cm^{-1} . The data set contains rotationally excited energy levels for all the 63 vibrational states which have been characterized by high resolution spectroscopy. The potential energy function obtained in the present work improves drastically the agreement with experiment for the highly excited local mode stretching states above $20\,000\text{ cm}^{-1}$. For the vibrational band origins of these states, the highest of which is measured at $25\,118\text{ cm}^{-1}$, our previous fitted potential produced discrepancies of more than 100 cm^{-1} . These deviations are reduced to less than 1 cm^{-1} by the potential energy function of the present work. We show that no significant improvement of the fit can be obtained by extending the analytical expression for the potential energy by further high-order terms. An analysis of the residuals shows that at the level of accuracy achieved, the major contribution to the error originates in the neglect of nonadiabatic correction terms in the Born-Oppenheimer kinetic energy operator. We conclude that any further improvement of the potential energy surface requires that such correction terms be included in the Hamiltonian. With the present potential, reliable extrapolations towards higher rotational and vibrational energies can be carried out, and we expect that such calculations can be very helpful in the assignment of experimental spectra involving highly excited states.

^aO. L. Polyansky, P. Jensen and J. Tennyson, *J. Chem. Phys.* **101**, 7651 (1994)

TC03

15 min 9:04

Fitting of a PES for rovibrational calculations on NO₂

Jeremy H. Schryber, Oleg Polyansky, Jonathan Tennyson, *Department of Physics and Astronomy, University College London, Gower Street, London WC1E 6BT*; Per Jensen, *Physikalisch-Chemisches Institut, Justus-Liebig-Universität Giessen, Heinrich-Buff-Ring 58, D-35392 Giessen, Germany*.

We took the potential energy surface for the ground electronic state of NO₂ constructed by Tashkun and Jensen^a using the MORBID Hamiltonian and computer program. We wished to fit this to experimental data using the exact kinetic energy (EKE) operator. Initially, EKE calculations were not possible due to the presence of holes in the surface. A better starting point for the fit was constructed using the method in Polyansky et al^b whereby MORBID and EKE calculations are combined. We then improved the surface by fitting it to available experimental data using an iterative least-squares fitting procedure. In the low-energy region (<10,000 cm⁻¹) the fitting was successful. Above approximately 10,000 cm⁻¹ the higher electronic state begins to perturb the vibrational energy levels of the ground state. We were unable to fit the surface well to the experimental data above 10,000 cm⁻¹. We aim to provide a surface which will give accurate rovibrational levels of NO₂.

^aS.A. Tashkun and P. Jensen, *J. Mol. Spec.*, **165**, 173-184 (1994).

^bO.L. Polyansky, P. Jensen and J. Tennyson, *J. Chem. Phys.*, **101**, 7651-7657 (1994).

TC04

15 min 9:21

VIBRATIONAL ENERGY REDISTRIBUTION (IVR): NEW MODELS AND COMPUTATIONAL APPROACHES

MARTIN GRUEBELE, *Department of Chemistry and Beckman Institute for Advanced Science and Technology, University of Illinois, Urbana, IL 61801*.

A deterministic model for IVR, which incorporates arbitrarily high order resonances via a scaling and factorization law for the vibrational matrix elements, is discussed. We also derive from this a "statistical vibrational triangle rule model," which takes into account the changes in dynamics during the progression from regular to chaotic spectra. In many practical cases under experimental study, highly vibrationally excited molecules fall into this intermediate regime. The models make a variety of simple predictions about the dilution factor, IVR rate, fraction of occupied phase space (Heller's F) as a function of energy, state density, molecular anharmonicity, and various other parameters. These are compared to both ultrafast and high-resolution IVR experimental data.

To evaluate IVR spectra or survival probabilities from these models, large scale computations on semi-sparse matrices of dimension 10,000-100,000 are required. These present a formidable challenge even for supercomputers using standard algorithms, such as Lanczos eigenvector calculations. We discuss symplectic propagators and the "matrix fluctuation-dissipation" (or MFD) theorem. These allow efficient computation of exact spectra, survival probabilities, and rates without full knowledge of the eigenfunctions.

TC05

15 min 9:38

APPROXIMATE SCALING OF MATRIX ELEMENTS FOR MULTIDIMENSIONAL ANHARMONIC VIBRATIONAL POTENTIALS

DANE MADSEN AND MARTIN GRUEBELE, *School of Chemical Sciences and Beckman Institute for Advanced Science and Technology, University of Illinois, Urbana, IL 61801.*

The intermediate vibrational energy regime - well above the zero point, yet below the dissociation limit - plays an important role in many molecular processes, such as radiationless transitions or intramolecular vibrational relaxation (IVR). For molecules with $N > 6$ vibrational degrees of freedom, the calculation of matrix elements, energy levels, and spectra of the fully anharmonic vibrational Hamiltonian at high energies presents a formidable problem. Here we derive an asymptotic formula based on the global topology of molecular potentials: under certain very general conditions the potential can be exactly factorized as N approaches infinity. Applying corrections derived from the $N=1$ limit yields several simple models for high-order force fields and matrix elements, which rely only on input parameters such as vibrational frequencies and cubic anharmonicities. Comparison of the models with numerical force fields derived from curvilinear model potentials and with Monte-Carlo sampled *ab-initio* calculations for several small molecules shows that they are useful asymptotic approximations for N as low as 3 or 6. Implications of these simple yet physically reasonable force fields for several recently developed models for IVR are discussed, in particular threshold effects of high order force-constants on energy redistribution.

TC06

15 min 9:55

A "MULTI-MOLECULE" RITZ PROGRAM

Giovanni Moruzzi, *Dipartimento di Fisica dell'Università di Pisa, Piazza Torricelli 2, I-56126 Pisa, Italy.*

The "Ritz" program, already presented in two previous Columbus Symposia ^{a b}, has been extended to enable the treatment of molecules other than methanol and its isotopomers. The new program first reads an ASCII file with information specific to the molecule (quantum numbers, transition rules, approximate wavenumbers for the vibrational modes ...), then loads the databases for the molecule and enters an interactive mode. As the older "Ritz" program, the new "multi-molecule" Ritz program evaluates the energy levels involved in the assigned lines by the Rydberg-Ritz combination principle, then extrapolates the energies of new levels by parabolic extrapolation, or searches for them by "expert system" techniques. The program has already been tested with an investigation of the small-amplitude vibrational ground state of hydrazine. Full investigations of the IR-FIR hydrazine spectrum (in collaboration with Li-Hong Xu) and cyanamide and methyl-amine spectra (in collaboration with the Physikalisches-Chemisches Institut of the University of Giessen) are planned.

^aG. Moruzzi and L. H. Xu, Ohio State University 49th International Symposium on Molecular Spectroscopy, TD04, p.122 (1994).

^bG. Moruzzi and L. H. Xu, Ohio State University 50th International Symposium on Molecular Spectroscopy, FA02, p.325 (1995).

Intermission

TC07**15 min 10:25****PATTERN RECOGNITION BY EXTENDED AUTO- AND CROSS-CORRELATION**

STEPHEN L. COY, MATTHEW P. JACOBSON, AND ROBERT W. FIELD, *Department of Chemistry, Massachusetts Institute of Technology, Cambridge, MA 02139.*

The traditional approach to understanding the information encoded in spectroscopic data has been first to assign each transition observed and then to relate the positions and intensities of the transitions to a model that allows insight into the system being studied. In complex and congested spectra, however, the process of assignment may be difficult, tedious, or even impossible. In such a situation, it is often desirable to be able to recognize patterns that are obscured by the complexity of the spectrum. For this purpose, we have developed two closely related pattern recognition techniques, which we refer to as Extended Autocorrelation (XAC) and Extended Cross-Correlation (XCC). The XAC can be used to locate patterns that are parameterized in a complex way within a congested spectrum. The XCC recognizes patterns that are common among two or more spectra. Tests of these techniques using synthetic spectra will be presented, as well as applications to the mass spectra of large molecules (XAC) and FTIR spectra of mixtures of deuterated ammonia isotopomers (XCC).

TC08**15 min 10:42****The Computation of Rotational and Vibrational Spectrum of Van Der Waals Molecules on Cray-T3D**

X. T. Wu, P. Korambath, E. F. Hayes, Zdenko Tomašić and Danny Sorensen, *Dept. of Chemistry, The Ohio State University, Columbus, OH 43210*; Zdenko Tomašić and Danny Sorensen, *Dept. of Mathematical Sciences, Rice University, Houston, TX 77251.*

The bound states of Van Der Waals Molecules are computed using iterative eigenvalue solver Implicitly Restarted Lanczos Method (IRLM). In this application two techniques are used to make the calculation more efficient. First Chebychev preconditioning is used to speedup the convergence. Secondly tensor product technique is used to calculate the sparse matrix - vector multiplication through dense matrix - matrix multiplications. The result program is many times faster than eispack routines. The parallelization of the program on Cray-T3D shows that the program also scales well on multi-processor supercomputers.

TC09**15 min 10:59****A SEMIEMPIRICAL PES FOR Kr-HS**

Prakashan P. Korambath, X. T. Wu, E. F. Hayes, C. Carter and Terry. A. Miller, *Dept. of Chemistry, The Ohio State University, Columbus, OH 43210.*

A semiempirical potential energy surface for Kr-HS van der Waals type molecule will be presented. The nature of the PES is similar to that proposed for Ar-HO by Bowman and co-workers [1]. The parameters in the Ar-HO surface was modified using an efficient nonlinear fit program to agree with experimental measurements for Kr-HS molecule by Miller and co-workers [2]. The calculated results will be reported along with comparisons with the experimental results of Miller and co-workers. Quantitative insights into the interaction potentials for similar systems will be discussed.

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1. J. M. Bowman, B. Gazdy, P. Schafer, M. C. Heaven. *J. Phys. Chem* **94** 2226 (1990).
 2. Private communication from T. A. Miller, Ohio State University.

TC10

10 min 11:16

ANALYSES OF VIBRATIONS OF Ar_n AND Ar_nCO_2 CLUSTERS BY MOLECULAR DYNAMICS CALCULATION

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 M. ICHIHASHI, T. KONDOW, *Department of Chemistry, School of Science, The University of Tokyo, Bunkyo-ku, Tokyo 113, Japan*; AND K. KUCHITSU, *Department of Chemistry, Faculty of Science, Josai University, Sakado, Saitama 350-02, Japan*.

Previously, we analyzed intracluster vibrational motions of Ar_n , $n=13-55$, clusters by use of molecular dynamics method ^a. It was shown that a number of collective vibrations were excited. The vibrations were assigned to breathing, quadruple spheroidal and quadruple torsional vibrations corresponding to the modes of a dense sphere with the radius of Ar_n and the phonon velocities in solid Ar. Such vibrations were observed for Ar clusters by the energy loss of colliding He atoms ^b. The frequencies of these vibrations were found to decrease with the increasing cluster size, suggesting that these vibrational motions are new physical properties of clusters obeying a scaling law.

In this work, the motions of Ar atoms and CO_2 molecule in Ar_nCO_2 cluster produced by addition of CO_2 to the surface of Ar_n cluster, are simulated by use of the classical molecular dynamics method. The potential is calculated by overlapping two-body Lennard-Jones potentials, where an anisotropic potential is used for the Ar- CO_2 interaction. By extracting the breathing and quadruple spheroidal vibrations, the frequencies of these modes are calculated to be: e.g., 33 and 20 cm^{-1} , respectively, for $\text{Ar}_{13}\text{CO}_2$. These values are almost identical to those for Ar_{13} . This indicates that the addition of CO_2 causes little effect on the vibration of Ar_{13} when the CO_2 molecule is on the surface of Ar_{13} . Cluster-temperature and cluster-size dependence of the frequencies will be presented.

^aY. Ozaki, M. Ichihashi and T. Kondow, *Chem. Phys. Lett.* 182, 57 (1991); *ibid.* 188, 555 (1992).

^bU. Buck and R. Krohne, *Phys. Rev. Lett.* 73, 947 (1994).

TC11

15 min 11:28

Ab Initio Vibrational Splittings for Hydrogen Atom Transfer in $\text{HO}_2^-/\text{O}_2\text{H}^-$ Isomerization

Wai-To Chan and Ian P. Hamilton, *Department of Chemistry, Wilfrid Laurier University, Waterloo, Ontario..*

A potential energy surface covering the interconversion between the two symmetry-equivalent geometries of the hydroperoxyl anion, HO_2^- via a symmetric T-shaped saddle point was computed at the QCISD(T)/6-311++G(2df,pd) level of theory. An analytical molecular potential function was fit to the *ab initio* data. The classical barrier to the interconversion was estimated to be 6057 cm^{-1} . Using the parameterized function the vibrational states were calculated by the discrete variable representation-distributed Gaussian basis method. Computations predict the onset of tunnelling from about 4 quanta in the bending mode-A splitting of 6 cm^{-1} is observed between the odd and even 040 state. Presence of at least one quanta in the O-O stretching mode enhances splitting significantly.

AB INITIO STRUCTURES, VIBRATIONS, AND THERMOCHEMISTRY OF IO, IO⁻, AND IO⁺

P. HASSANZADEH^a AND K. K. IRIKURA, *Physical and Chemical Properties Division, National Institute of Standard and Technology, Gaithersburg, MD 20899.*

Ab initio internuclear distances and anharmonic constants for IO, IO⁻, and IO⁺ were calculated at the CCSD(T) level using 6-311+G(3df,2p) basis sets. The reliability of the calculations was tested against the available experimental values for IO and IO⁻.

Electronic energies were also calculated at the CCSD(T) level using the 6-311+G(3df,2p) basis sets, Sadlej's polarized basis sets (PBS), and Wadt and Hay's effective core potential (ECP) basis sets at the experimental geometries and corrected by the experimental zero-point vibrational energies. The enthalpy of formation of the hypoiodite anion IO⁻ (¹Σ⁺) ($\Delta_f H_0^\circ$ -109 ± 5 kJ/mol, uncertainties are 2σ) was obtained from *ab initio* energetics for the metathesis reactions IO⁻ + Cl⁻ → ClO⁻ + I⁻ and IO⁻ + Cl₂ → ClO⁻ + ICl. The reliability of the computational procedure was tested by performing analogous calculations for BrO⁻ and comparing the results with the accepted value for the enthalpy of formation of BrO⁻.

The enthalpy of formation for IO (X²Π_{3/2}) ($\Delta_f H_0^\circ$ = 120 ± 5 kJ/mol) was deduced from the calculated $\Delta_f H_0^\circ$ (IO⁻) and the experimental electron affinity of IO (EA = 229.43 ± 0.06 kJ/mol) measured by Gilles et al.. The enthalpy of formation of IO⁺(³Σ⁻) ($\Delta_f H_0^\circ$ = - 1060 ± 5 kJ/mol) was also derived from the present enthalpy of formation of IO and the experimental adiabatic ionization energy of IO (IE = 939.4 ± 1.7 kJ/mol) measured by Zhang et al. The corresponding bond dissociation energies are D₀^o(IO)= 167 ± 5 kJ/mol, D₀^o(IO) = 234 ± 5 kJ/mol, and D₀^o(IO⁺)= 303 ± 5 kJ/mol.

JANAF-style thermodynamic functions for IO, IO⁻, and IO⁺ from 0 to 1000 K are also tabulated.

^aGuest Researcher

TD01

15 min 8:30

THE STRUCTURE OF HALOGEN DIMERS: MICROWAVE SPECTRUM OF (ClF)₂

K. HIGGINS, W. KLEMPERER, *Department of Chemistry, Harvard University, Cambridge, MA 02138*; F.-M. TAO, *Department of Chemistry, California State University, Fullerton, CA 92634*; E. ARUNAN, *Department of Chemistry, Indian Institute of Technology, Kanpur 208016, India*; T. EMILSSON, H.S. GUTOWSKY, *Department of Chemistry, University of Illinois, Urbana IL 61801*.

The rotational spectrum of (ClF)₂ is reported. The molecule is a slightly asymmetric prolate rotor. A number of transitions have been observed for the four isotopomers. A very detailed study of the $J = 1 \leftarrow 0$ transitions provides precise values for the rotational constants $\frac{B+C}{2}$ as well as hyperfine structure constants $eqQ_{aa}(\text{Cl})$. A series of a-type transitions up to $J = 7$ are observed under somewhat lower resolution. We also observe several b-type transitions with $K = 1 \leftarrow 0$.

Preliminary values of the rotational constants for the (³⁵ClF)₂ isotopomer are $A = 21722$, $B = 1111.7$, $C = 1055.7$ MHz. These values may be compared to the rotational constants calculated from the minimum energy geometry obtained at the MP2 level: $A = 21654$, $B = 1121$, $C = 1066$ MHz. The geometry is planar with the center of mass separation 3.89 Å. The array FCl...F is almost linear and the angle between the two FCl units is 111°. The complex appears to be quite rigid. The experimental hyperfine structure constants for the (³⁵ClF)₂ isotopomer are $eqQ_{aa}(\text{Cl}_1) = -123.9$ MHz and $eqQ_{aa}(\text{Cl}_2) = -6.72$ MHz. Constants calculated from the MP2 geometry by projecting the monomer $eqQ(\text{Cl})$ values to the inertial axes are in good agreement with experiment.

The crystal structure of ClF appears to be presently undetermined. A comparison of (Cl₂)₂ calculated at a level similar to (ClF)₂ is compared with the crystal structure of Cl₂.

TD02

15 min 8:47

THE INTERMOLECULAR POTENTIAL SURFACE OF INERT GAS HALOGEN COMPLEXES AS PROBED BY HeClF

K. HIGGINS, W. KLEMPERER, *Department of Chemistry, Harvard University, Cambridge, MA 02138*; F.-M. TAO, *Department of Chemistry, California State University, Fullerton, CA 92634*.

We report the intermolecular potential of HeClF as studied by *ab initio* theory and microwave spectroscopy. The potential surface was calculated at the MP4 level and is characterized by three minima, the deepest of which is -58.1 cm at 0° and 3.57 Å, the next is -35.2 cm⁻¹ at 110° and 3.30 Å, and the shallowest is -32.3 cm⁻¹ at 180° and 3.95 Å. The rotation-vibration levels calculated from the *ab initio* potential fall into three categories with the He atom localized in each of the three minima. These configurations can be viewed as different isomeric forms or as vibrational states of HeClF. Pure rotational transitions have been observed for the two lowest energy vibrational states (linear and T-shaped) and these are in good agreement with predictions from the *ab initio* surface. Two linear → T-shaped transitions have been observed for the complex. The observed vibrational interval between the linear and the T-shaped forms differ from predictions by 0.9 cm⁻¹. The nuclear hyperfine structure and electric dipole moments measured are also in good agreement with those calculated from the *ab initio* surface. The potential surface with multiple minima observed here appears to be a general phenomena for inert gas halogen complexes. This is the first experimental observation of both a linear and a T-shaped form for this kind of complex.

Spectroscopic constants for the linear form of He³⁵ClF are $B = 5586.389(7)$ MHz, $D = 1.367(1)$ MHz, $eqQ_{J=1} = -133.70(6)$ MHz, $eqQ_{J=2} = -133.79(6)$ MHz and $\mu = 0.880(1)$ D. Constants for the T-shaped form are $B = 7042.256(12)$ MHz, $eqQ_{J=1} = -40.02$ MHz, $eqQ_{J=2} = -50.33$ MHz and $\mu = 0.614(7)$ D.

TD03

15 min 9:04

FOURIER TRANSFORM MICROWAVE SPECTROSCOPY OF $\text{Ar-N}_2\text{O}$ AND $\text{HCCH-N}_2\text{O}$, HELEN O. LEUNG and DEEPA GANGWANI, Department of Chemistry, Mount Holyoke College, South Hadley, MA 01075.

The rotational spectra of two N_2O complexes, $\text{Ar-N}_2\text{O}$ and $\text{HCCH-N}_2\text{O}$, have been studied using a pulsed-nozzle Fourier transform microwave spectrometer of the Balle-Flygare type in the 8 - 16 GHz region. Although the rotational spectrum of $\text{Ar-N}_2\text{O}$ was first observed by Klemperer and coworkers,¹ each rotational transition took many hours of signal averaging and yet the hyperfine components were not resolved. Thus, the spectroscopic constants and structural parameters were not well determined. Likewise, because the dimer $\text{HCCH-N}_2\text{O}$ was observed by Muentner and coworkers² in the infrared, no hyperfine structure was resolvable. We have observed 7 rotational transitions for $\text{Ar-N}_2\text{O}$ (2 are *a* type and 5 are *b* type) and 17 transitions for $\text{HCCH-N}_2\text{O}$ (8 are *a* type and 9 are *b* type). The spectral lines are split into many hyperfine components due to the presence of the two quadrupolar ^{14}N nuclei. The spectra are analyzed using the Watson A-reduced Hamiltonian with the inclusion of hyperfine interactions to yield accurate spectroscopic parameters and angular information.

¹C. H. Joyner, T. A. Dixon, F. A. Baiocchi, and W. Klemperer, *J. Chem. Phys.* **75**, 5285 (1981).

²T. A. Hu, L. H. Sun, and J. S. Muentner, *J. Chem. Phys.* **95**, 1537 (1991).

TD04

15 min 9:21

Direct Absorption Observation of the van der Waals Bending Band of ArHCN by Millimeterwave Spectroscopy Combined with Pulsed-jet Expansion Technique. Extension to the $j = 2 - 1$ hot band.

Keiichi Tanaka, Keisuke Uemura, and Mitsuaki Shirasaka

Millimeterwave spectrometer combined with a pulsed supersonic jet nozzle was applied to observe the absorption spectra of the van der Waals bending band of ArHCN in the 150 - 270 GHz region. The transitions near band origin have been studied by EROS and the band origins were reported [1]. Seventeen rovibrational transitions split into hyperfine structure due to the nitrogen nucleus were newly observed for both subband $\Sigma_1 - \Sigma_0$ and $\Pi_1 - \Sigma_0$ of the $j = 1 - 0$ fundamental band. An improved set of molecular constants, including the band origins, rotational constants, quadrupole coupling constants, and the Coriolis coupling constant between the Σ_1 and Π_1 bending substates, was determined.

More than one hundred of rather weak lines, of which intensities are about one third or less of the $j = 1 - 0$ fundamental lines, were observed. These lines are due to the hot band ($j = 2 - 1$ and $3 - 2$) transitions of the vdW bending transitions. Some of the lines are tentatively assigned to the *R*-branch lines of the $\Sigma_2 - \Pi_1$ band. Further analysis will give us the molecular structure in the excited state of vdW bend mode.

[1] S. Drucker, A. L. Cooksy, and W. Klemperer, *J. Chem. Phys.* **95**, 5158 (1991).

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TD05

10 min 9:38

THE MICROWAVE SPECTRUM AND STRUCTURE OF THE CARBON DIOXIDE-SULFUR DIOXIDE COMPLEX, Department of Chemistry, The University of Michigan, Ann Arbor, MI 48109-1055; L. SUN, I. I. IOANNOU, and R. L. KUCZKOWSKI.

The rotational spectra of nine isotopomers of the carbon dioxide - sulfur dioxide van der Waals complex were observed with a pulsed molecular beam Fourier transform microwave spectrometer. All odd K energy levels were missing in the symmetric isotopic species, but were present in the singly substituted $C^{18}O^{16}O$ or $S^{34}O^{16}O$ isotopomers. No inversion splittings were observed in any of the isotopic species. The observed frequencies for each isotopomer were fit to obtain rotational and centrifugal distortion constants. Consideration of the moments of inertia, selection rules and missing levels indicate that the complex has a cross structure with C_{2v} symmetry. The C_2 axis of SO_2 is perpendicular to the C_∞ axis of CO_2 . The negative end of the SO_2 dipole moment points to the carbon atom. The center of mass distance between the two monomers is $3.29(5)$ Å. The dipole moment is $1.771(2)$ D. Distributed multipole electrostatic calculations support the cross structure.

TD06

15 min 9:50

MICROWAVE SPECTRUM AND STRUCTURE OF HNO_3-H_2O , M. CANAGARATNA, J.A. PHILLIPS, M. OTT, AND K.R. LEOPOLD, Department of Chemistry, University of Minnesota, Minneapolis, MN 55455.

The microwave spectrum of HNO_3-H_2O and six of its isotopic derivatives have been investigated by pulsed-nozzle Fourier transform microwave spectroscopy. The complex has a cyclic, doubly hydrogen bonded structure with a coplanar arrangement of the heavy atoms. One of the water protons lies above the plane. A near-linear hydrogen bond, 1.76 Å in length, is formed between the proton of the HNO_3 and the oxygen of the H_2O . A longer (2.76 Å) hydrogen bond between one of the water protons and an oxygen of the HNO_3 completes the ring. The dimer was produced by continuously evaporating liquid water into a pulsed expansion of HNO_3 in Ar, and evidence is presented for extensive H/D isotopic scrambling during experiments using $H_2O + DNO_3$ or $D_2O + HNO_3$. The results are compared with recent *ab initio* calculations.

Intermission

TD07

15 min 10:20

GAS PHASE STRUCTURE OF A FRIEDEL-CRAFTS INTERMEDIATE: MICROWAVE SPECTRUM OF $\text{CH}_3\text{F}\cdot\text{BF}_3$, L.A. PHILLIPS, M. CANAGARATNA, M. OTT, AND K.R. LEOPOLD, Department of Chemistry, University of Minnesota, Minneapolis, MN 55455.

The rotational spectrum of $\text{CH}_3\text{F}\cdot\text{BF}_3$ has been observed via pulsed-nozzle Fourier transform microwave spectroscopy. A dense spectrum is observed, and transitions arising from two internal rotor states of the complex have been identified. The spectra are consistent with the expected geometry in which the fluorine of the CH_3F approaches the BF_3 on or near its C_3 axis, with a B--F-C angle of 120° . The intermolecular B--F bond length is about 2.4 \AA , a value considerably shorter than both the 2.7 \AA distance expected for a van der Waals bond length and the 2.54 \AA distance previously observed in $\text{HF}\cdot\text{BF}_3$. Complexes of this type have been invoked as intermediates in solution phase Friedel-Crafts alkylation reactions, and the relevance of the current observations to this chemistry will be discussed.

TD08

15 min 10:37

THE ROTATIONAL SPECTRUM OF ARGON-SILANE, Y. KAWASHIMA, Department of Chemical Technology, Kanagawa Institute of Technology, Atsugi, Kanagawa 243-02, Japan; R. D. SUENRAM, G. T. FRASER, and F. J. LOVAS, Optical Technology Division, National Institute of Standards and Technology, Gaithersburg, MD 20899 and E. HIROTA, The Graduate University for Advanced Studies, Hayama, Kanagawa, 240-01, Japan

Microwave spectra of $\text{Ar}\cdots^{28}\text{SiH}_4$, $\text{Ar}\cdots^{29}\text{SiH}_4$, and $\text{Ar}\cdots^{30}\text{SiH}_4$ have been measured using a pulsed-nozzle Fourier-transform microwave (FTMW) spectrometer. The $K=0$ and $K=1$ components of the $J=3 \leftarrow 2$ through the $J=7 \leftarrow 6$ transitions have been measured and assigned in the 9 - 24 GHz region. For the primary isotopic species, $\text{Ar}\cdots^{28}\text{SiH}_4$, two $K=0$ (A and F symmetry) and three $K=1$ (E and F symmetry) rotational progressions are observed at the 1 K rotational temperature of the supersonic expansion. The rotational constant for the $K=0$, A state is $B=1700.40624(9) \text{ MHz}$ and the centrifugal distortion constants are, $D_J=29.089(3) \text{ kHz}$ and $H_J = -1.91(3) \text{ Hz}$, where the number in parentheses represents one standard deviation from the fit. The values of the rotational constants for the $K=0$ A and F states and for $K=1$ E states are in good agreement with the infrared determined values for $\text{Ar}\cdots^{28}\text{SiH}_4$.^a The Stark effects of the E state transitions are first order, yielding a dipole moment for $\text{Ar}\cdots^{28}\text{SiH}_4$ of 0.027 D . The splitting of the $K=1$, F state provides an estimate of the barrier to internal rotation of the SiH_4 moiety of $\sim 60 \text{ cm}^{-1}$.

^aR.W. Randall, J.B. Ibbotson, and B.J. Howard, J. Chem. Phys., **100**, 7051-7060 (1994).

TD09

15 min 10:54

Microwave spectrum of the Xe-propyne Van der Waals complex

Th. Brupbacher, W. Jäger^a, M. C. L. Gerry, *Department of Chemistry, University of British Columbia, Vancouver, B.C., V6T 1Z1, Canada*; D. F. Eggers †, *Department of Chemistry, University of Washington, Seattle, WA 98195, U. S. A.*

The microwave spectrum of the Xe-propyne Van der Waals complex has been recorded between 4–22 GHz, using a newly-developed pulsed molecular beam Fourier transform microwave spectrometer incorporating automated frequency scanning. The spectra of five isotopomers, involving ¹²⁹Xe, ¹³¹Xe, ¹³²Xe, ¹³⁴Xe, and ¹³⁶Xe, were observed in natural abundance.

The geometry of Xe-propyne is T-shaped, comparable to that of Ar-propyne^b. Hindered internal rotation of the methyl group in propyne splits the levels into A and E species. The A species transitions could be analysed using predictions from an on-going analysis of the infrared spectrum^c. The microwave spectrum was analysed using a rotation-internal rotation Hamiltonian. The barrier to internal rotation V_3 was found to be $\sim 22\text{cm}^{-1}$, comparable to that of Ar-propyne.

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^bT. A. Blake *et al.*, J. Chem. Phys., **98**, p. 6031 (1993)

^cR. O. Watts, T. A. Blake, P. Muino and D. F. Eggers †, private communication

TD10

15 min 11:11

FOURIER TRANSFORM MICROWAVE SPECTROSCOPY OF ARGON CYCLOBUTANONE

MICHAEELEEN R. MUNROW, WEI CHEN, WALLACE C. PRINGLE, and STEWART E. NOVICK,
Department of Chemistry, Wesleyan University, Middletown, CT 06459.

The microwave spectroscopy of the Ar cyclobutanone van der Waals complex and cyclobutanone monomer have been obtained in a pulsed jet Fourier transform microwave spectrometer. The effect of van der Waals bonding on the ring puckering vibration will be discussed. In addition, the hyperfine splitting due to the methylene protons has been observed in both the complex and the monomer.

TD11

15 min 11:28

ROTATIONAL SPECTRA OF $\text{CH}_3\text{CCH-NH}_3$, NCCCH-NH_3 , AND NCCCH-OH_2

A.R. Hight Walker, R. Omron, G.T. Fraser, R.D. Suenram, *Optical Technology Division, National Institute of Standards and Technology, Gaithersburg, MD 20899*; G. Hilpert, *Institut für Angewandte Physik, Universität Bonn, Wegelerstraße 8, D-53115 Bonn, Germany*.

Microwave spectra of NCCCH-NH_3 , $\text{CH}_3\text{CCH-NH}_3$, and NCCCH-OH_2 have been recorded using a pulsed-nozzle Fourier-transform microwave spectrometer. The complexes, NCCCH-NH_3 and $\text{CH}_3\text{CCH-NH}_3$, are found to have symmetric-top structures with the acetylenic proton hydrogen-bonded to the nitrogen of the NH_3 . The data for $\text{CH}_3\text{CCH-NH}_3$ are further consistent with free or nearly free internal rotation of the methyl top against the ammonia top. For NCCCH-OH_2 , the acetylenic proton is hydrogen-bonded to the oxygen of the water. The water complex has a dynamical C_{2v} structure, as evidenced by the presence of two nuclear-spin modifications of the complex. The hydrogen-bond lengths and hydrogen-bond stretching force constants are 2.212 Å and 10.8 N/m, 2.322 Å and 6.0 N/m, and 2.125 Å and 9.6 N/m, for NCCCH-NH_3 , $\text{CH}_3\text{CCH-NH}_3$, and NCCCH-OH_2 , respectively. For the cyanoacetylene complexes, these bond lengths and force constants lie between the values for the related hydrogen cyanide and acetylene complexes of NH_3 and H_2O . The NH_3 bending and weak-bond stretching force constants for $\text{CH}_3\text{CCH-NH}_3$ are less than those found in NCCCH-NH_3 , NCH-NH_3 , and HCCH-NH_3 , suggesting that the hydrogen bonding interaction is particularly weak in $\text{CH}_3\text{CCH-NH}_3$. The weakness of the bond is partially a consequence of the orientation of the monomer electric dipole moments in the complex. In $\text{CH}_3\text{CCH-NH}_3$ the antialigned monomer dipole moments leads to a repulsive dipole-dipole interaction energy, while in NCH-NH_3 and NCCCH-NH_3 the aligned dipoles give an attractive interaction.

TD12

15 min 11:45

FOURIER TRANSFORM MICROWAVE SPECTROSCOPY OF TRIMETHYLENE SULFIDE MONOMER AND ARGON VAN DER WAALS COMPLEX IN THE RING-PUCKERING GROUND INVERSION STATES, W. C. PRINGLE, M. R. MUNROW, W.D.R. PREMASIRI, D.W. MCCAMANT, WEI CHEN, S. E. NOVICK, Department of Chemistry, Wesleyan University, Middletown, CT 06459

Over 30 lines of the ground states inversion-rotation spectrum of trimethylene sulfide monomer have been measured to 5 kHz resolution in a Balle-Flygare pulsed nozzle, molecular beam Fourier transform microwave spectrometer. A Hamiltonian with Coriolis coupling, inversion splitting, rotational constants and centrifugal distortion constants for each inversion level will be discussed. The hyperfine spectrum due to the methylene hydrogens has also been observed. The use of the perturbations of the ring-puckering potential to study Van der Waals bonding will be discussed.

TE01

30 min 1:30

TOWARDS THE ULTIMATE OPTICAL DETECTION SENSITIVITY: NEW SPECTROSCOPIC OPPORTUNITIES - AND A ZILLION NEW WAVELENGTH/FREQUENCY STANDARDS

JOHN HALL, JILA, NIST & Dept of Chemistry & Biochemistry, Univ. of Colorado, Boulder, CO 80309.

High sensitivity detection of quantum absorption is demonstrated at a sensitivity of 1×10^{11} integrated absorption, in 1 sec, using 10 mTorr total gas pressure. Achieving highly sensitive detection relies on simple, basic principles: 1) The molecule-generated electric field in the forward direction (the "darkness wave") is most precious, and contains the maximum available information. It is the physical manifestation of the $-\alpha^*L$ term appearing when Beer's absorption law is expanded for low opacity. 2) After generating the molecular signal, the detected unabsorbed light sets the "shotnoise" measurement floor. We use an optical transmission cavity for the gas cell, since the high internal "build-up" field will elicit a strong molecular "darkness wave," for a given transmitted dc light on the detector. A more conventional explanation of Cavity Enhancement would be the extension of the effective cell length by the factor $Finesse * 2/\pi$. 3) To avoid excess low-frequency noise, such small signals should be measured by ac methods, comparing on-resonant and off-resonant cases in quick succession. 4) By SIMULTANEOUSLY obtaining and subtracting these cases, one provides a signal channel with NO OUTPUT unless there is a resonance. This is conveniently accomplished by using the FM detection method with the optical heterodyne sidebands and carrier being transmitted through the cavity via adjacent axial orders. 5) A remarkable property of this configuration, when the modulation frequency = cavity mode spacing, is the suppression of ANY detection of laser frequency noise with the transmitted light. We can refer to this property as (laser FM-) Noise-Immune detection. This enables profitable use of cavity finesse in the range above 10,000, without a noise penalty. Altogether, we refer to this new spectroscopy as Noise-Immune, Cavity-Enhanced, Optical Heterodyne Molecular Spectroscopy, ie. "NICE OHMS". We have measured excellent saturated dispersion signals from HCCH in the band near 790 nm ($\nu_1 + 3 \nu_3$), and recently, using a Nd:YAG source, from the HCCD P(5) line ($\nu_2 + 3 \nu_3$) at 1064 nm. The saturation peaks broaden from the transit limit of 270 kHz near zero pressure at the rate 34.7 kHz/mTorr. We observe interesting narrow linewidths 8-fold below the transit limit, basically using optical selection of slow molecules by low power and pressure (2 mW and 2 mTorr). The absolute frequency is measured to be $281,635,363.960 \text{ MHz} \pm 45 \text{ kHz}$.

TE02

10 min 2:05

NEW NEAR-INFRARED TRANSIENT ABSORPTION TECHNIQUES, BOR-CHEN CHANG AND TREVOR J. SEARS, Department of Chemistry, Brookhaven National Laboratory, Upton, New York 11973-5000.

A new combination of transient frequency-modulation (FM) absorption and supersonic jet expansion has been developed to study the spectroscopy of free radicals. This technique has been successfully demonstrated in obtaining jet-cooled $\tilde{A} \leftarrow \tilde{X}$ spectra of NH_2 and HCCl . In addition, a simultaneous acquisition of temporal waveform in frequency scan reveals interesting information on the velocity and density distributions of supersonic jet expansion systems. Results obtained using a pinhole nozzle and a slit nozzle show the characteristic differences between these two jet systems. The details of this technique will be presented. We have also recently used a new diode laser system to study the high resolution electronic spectroscopy of free radicals and preliminary results will be presented.

Acknowledgment: This work was carried out under Contract No. DE-AC02-76CH00016 with the U.S. Department of Energy and supported by its Division of Chemical Sciences, Office of Basic Energy Sciences.

TE03**15 min 2:17**

TRANSIENT FM SPECTROSCOPY FOR DOPPLER MEASUREMENTS OF PHOTOFRAGMENT VELOCITIES AND VECTOR CORRELATIONS, SIMON W. NORTH AND GREGORY E. HALL, Department of Chemistry, Brookhaven National Laboratory, Upton, NY 11973-5000

Doppler-broadened FM line profiles of nascent photoproducts have been measured for several photodissociation systems. We describe methods required for the quantitative analysis of the FM line shapes to give velocity and rotational polarization information. Correlated state distributions and velocity-dependent vector correlations can be extracted with relative ease from a set of high-quality line shapes.

Acknowledgment: This work was carried out under Contract No. DE-AC02-76CH00016 with the U.S. Department of Energy and supported by its Division of Chemical Sciences, Office of Basic Energy Sciences.

TE04**10 min 2:34**

THEORETICAL AND EXPERIMENTAL ADVANTAGES OF A COMPACT MIRAGE SPECTROSCOPY SETUP FOR TRACE GAS DETECTION

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We present the advantages of a compact setup for real time *in situ* trace gas detection based on photothermal deflection spectroscopy optimized for practical applications^a. The use of high quality Ge windows permits a true parallel geometry, resulting in a design resistant to ambient air motion while preserving the advantages the technique presents with respect to standard absorption spectroscopy, such as good sensitivity, local sample probing and open air measurement capability. We estimate the detection limit of C₂H₄ in an N₂ atmosphere to be 100 ppt, and have measured real time *in situ* emissions from a variety of solid and semisolid samples to evaluate environmental, industrial, and agricultural applications.

^aB. Zimering, A.C. Boccara, *Rev. Sci. Inst.* (in press)

TE05**15 min 2:46**

INTRACAVITY LASER ABSORPTION SPECTROSCOPY IN HIGHLY EXCITED OVERTONES OF HOCl: DENSITY OF STATES, INTRAMOLECULAR ENERGY REDISTRIBUTION, AND LIFETIMES

A. KACHANOV, *Laboratoire de Spectrométrie Physique Université J. Fourier/CNRS/Grenoble BP87 38402 Saint Martin d'Hères Cedex France*; B. ABEL, A. CHARVAT, H. HAMANN, S. A. KOVALENKO, AND J. TROE, *Institut für Physikalische Chemie der Universität Göttingen, Tammannstr.6, 37077 Göttingen.*

The spectra of coupled vibrational overtone states in polyatomic molecules are of fundamental interest for the understanding of (intra) molecular dynamics and related phenomena, such as unimolecular reaction and internal vibrational redistribution (IVR), as spectroscopy on these highly excited eigenstates probes the features of the intramolecular potential which is relevant to these processes.

Using a combined Ti:Sapphire/Ring-Dye intracavity laser absorption spectrometer having a spectral resolution of 0.008 cm⁻¹, we were able to record the overtone and combination bands of HOCl molecule in the 12000-17000 cm⁻¹ range.

For the states very close to the dissociation threshold it turned out to be possible to do spectroscopic assignments and determine molecular constants. We derived the energy dependence of the density of states from a Dunham expansion used for band origin predictions and representation of vibrational states. Fermi resonance perturbations leading to the onset of IVR were investigated. We will discuss the possibility of determination of the lifetimes from linewidth measurements near the dissociation threshold.

TE06

10 min 3:03

EXCITED STATE GAS PHASE SPECIES OBSERVED IN RADIOFREQUENCY PLASMAS STUDIED BY OPTICAL EMISSION AND INTRACAVITY LASER SPECTROSCOPY TECHNIQUES

Dean R. Peterman and James J. O'Brien, Department of Chemistry and Center for Molecular Electronics, University of Missouri-St. Louis, St. Louis, MO 63121-4499.

The intracavity laser spectroscopic (ILS) technique provides a very sensitive method that can be used to determine the number density of gas phase intermediate species associated with radiofrequency (RF) plasma discharges. It has been used to obtain the concentration and spatial distribution of excited state ($n=2$) atomic hydrogen (H^*) observed in RF plasmas of hydrogen and in hydrocarbon RF plasmas used in depositing diamond-like carbon films. The H^* is observed via the H_α profiles. Because of the high sensitivity of the ILS method, the H^* spectra can be obtained at very high spectral resolution. This enables study of the H_α profiles in considerable detail. Optical emission spectroscopy is used to examine emitting species such as excited state molecular hydrogen (H_2^*) and H^* . These *in situ* studies provide diagnostic data as well as information about the deposition mechanism.

TE07

15 min 3:15

EXPERIMENTAL STUDY OF ATOM FLUORESCENCE LINES IN THE LASER PRODUCED PLASMA

O. A. BUKIN, E. A. SVIRIDENKOV, *Lebedev Physical Institute, 53 Leninskii pr., Moscow Russia*; N. V. SUSHILOV and A. Yu. MAJOR, *Pacific Oceanological Institute, Russian Academy of Sciences, 43 Baltiyskaya, Vladivostok, 690041 Russia*.

Emission line shapes of laser plasma generated on the surface of an aluminium are studied experimentally. The shifts of the centers of self-reversed absorption lines with the wave length 3962 Å and 3944 Å are registered. Two physical mechanisms of these shifts are discussed.

TE/01

10 min 3:45

FOURIER TRANSFORM EMISSION SPECTROSCOPY OF THE $A^2\Sigma^+ - X^2\Pi$ TRANSITION OF SILVER MONOXIDE, M.K. SIEBER and L.C. O'BRIEN, Department of Chemistry, Southern Illinois University at Edwardsville, Edwardsville, IL 62026-1652.

The $A^2\Sigma^+ - X^2\Pi$ transition of AgO has been observed for the first time. The spectrum was observed at 8300 cm^{-1} , recorded in emission with the high resolution, Fourier transform spectrometer associated with the McMath-Pierce Solar Telescope at Kitt Peak. The excited AgO molecules were produced in a low pressure silver hollow cathode, using a slow flow of 0.8 Torr neon and 15 mTorr oxygen. Preliminary constants for the $A^2\Sigma$ state of AgO are: $T_0=8294.7\text{ cm}^{-1}$ $B=0.332\text{ cm}^{-1}$, $\gamma=0.037\text{ cm}^{-1}$. Preliminary constants for the $X^2\Pi$ state of AgO are: $A_{SO}=-269.9\text{ cm}^{-1}$ $B=0.309\text{ cm}^{-1}$, and $p=-0.022\text{ cm}^{-1}$. The silver isotope structure is resolved at high J (^{107}Ag 52%, ^{109}Ag 49%). The analysis of this transition will be presented.

TE/02

10 min 3:57

Emission Spectroscopy of Metal Fluorides: NaF and TiF

Alexandrina Muntianu, P. F. Bernath, *Center for Molecular Beams and Laser Chemistry, University of Waterloo, Waterloo, On., Canada, N2L 3G1*; R. S. Ram *Department of Chemistry, University of Arizona, Tucson, AZ 85721* and S. P. Davis *Department of Physics, University of California, Berkeley, CA 94720*

The high-resolution infrared emission spectrum of sodium monofluoride has been recorded with a Fourier transform spectrometer. A total of 1131 of vibration-rotation transitions, from the $v=1 \rightarrow 0$ to $v=9 \rightarrow 8$ vibrational bands, have been assigned. The infrared data have been combined with existing microwave data in order to obtain improved spectroscopic constants, including Dunham Y_{ij} and U_{ij} coefficients, for the $X^1\Sigma^+$ electronic ground state of NaF. The electronic spectrum of titanium monofluoride molecule was recorded using the same technique, and a preliminary analysis has been attempted.

TE/03

10 min 4:09

FOURIER TRANSFORM INFRARED EMISSION SPECTROSCOPY OF THE NEW $b^1\Pi - a^1\Sigma^+$ TRANSITION OF BN

R. S. RAM AND P. F. BERNATH

The emission spectrum of BN has been investigated in the $1800\text{--}10,000\text{ cm}^{-1}$ region using a Fourier transform spectrometer. BN was formed in a microwave discharge of He with a trace of BCl_3 and N_2 . The bands with Q-heads at 3339 , 3514 , 4827 and 5024 cm^{-1} have been assigned as the 1-1, 0-0, 2-1 and 1-0 bands of the $b^1\Pi - a^1\Sigma^+$ transition, analogous to the $A^1\Pi_u - X^1\Sigma_g^+$ (Phillips) system of the isoelectronic molecule C_2 . The rotational analysis of these bands has provided the molecular constants for the $b^1\Pi$ and $a^1\Sigma^+$ states. This work represents the first observation of the $b^1\Pi - a^1\Sigma^+$ transition of BN in gas phase.

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TE'04

15 min 4:21

CHARACTERISATION OF SEVERAL ELECTRONIC STATES OF FeH.

DAMIAN M. GOODRIDGE, DANIEL F. HULLAH, AND JOHN M. BROWN, *The Physical and Theoretical Chemistry Laboratory, South Parks Road, Oxford, UK, OX1 3QZ.*

FeH is an open shell diatomic molecule which has been identified in the atmospheres of cool stars from the observation of its electronic spectrum. Analysis of the spectrum provides insight into the nature of bonding and the coupling of angular momenta. Due to the abundance of unpaired electrons, the states of FeH have high orbital and spin angular momenta. The rotational constants for the electronic states observed are in the region of 5 to 6 cm^{-1} . These factors result in complex, many-line spectra where branch structure is difficult to pick out.

Three main systems have previously been identified: in the near infrared^a; the green^{b,c}; and the blue^d regions of the electromagnetic spectrum. The infrared system has been assigned to a $^4\Delta - ^4\Delta$ transition, where the lower $^4\Delta$ state is the ground state of FeH. More recently, lines in the blue system have been assigned as $g^6\Phi - X^4\Delta$ and $g^6\Phi - a^6\Delta$ transitions.

Rovibrational features in the green system have now been assigned to the $e^6\Pi - a^6\Delta$ transition. Dispersed fluorescence studies have resulted in the identification of two further systems at around 600 and 630nm. Rotational lines in the 630nm system have also been observed by laser induced fluorescence and assigned to the $e^6\Pi - c^6\Sigma$ transition. Work is currently underway to produce an analysis of both of these systems.

^aJ. G. Phillips, S. P. Davis, B. Lindgren, and W. J. Balfour *Astrophys. J. Supp.* **65**, 721 (1987).

^bP. K. Carroll, P. McCormack, and S. O'Connor, *Astrophys. J.* **208**, 903 (1976).

^cDavid A. Fletcher, Robert T. Carter, John M. Brown, and Timothy C. Steimle *J. Chem. Phys.* **93**, 9192 (1990).

^dRobert T. Carter and John M. Brown, *J. Chem. Phys.* **101**, 2699 (1994).

TE'05

15 min 4:38

Electronic Spectroscopy of RhH and RhD in the 430 - 470 nm Region

Jianying Cao, Walter J. Balfour, and Charles X. W. Qian, *Department of Chemistry, University of Victoria, P.O.Box 3065, Victoria, B.C., Canada, V8W 3P6.*

We report on our recent spectroscopic study of RhH and RhD. These molecules were generated in a laser vaporization molecular beam source and detected by laser induced fluorescence. Eight bands of RhD as well as two bands of RhH were observed for the first time in the 430 - 470 nm region. Rotational analyses have been carried out for all of the bands. The ground state has $\Omega'' = 3$ and is assigned to a $^3\Delta_3$ state, consistent with recent *ab initio* calculations. The electronic configuration of the ground state is believed to be $9\sigma^2 5\pi^4 2\delta^3 10\sigma^1$. The excited states (three of them have $\Omega' = 3$, one $\Omega' = 2$, and another $\Omega' = 4$) may arise from the $\{Rh^+ 4d^7 5s^1 ^3F\}$ supermultiplet ^a. The electronic structures of RhH and RhD are also compared with those of the isovalent CoH and CoD molecules ^b.

^aJ. A. Gray, M. Li, T. Nelis, and R. W. Field, *J. Chem. Phys.* **95**, 7164 (1991).

^bM. Barnes, A. J. Merer, and G. F. Metha, *J. Mol. Spectrosc.* **173**, 100 (1995).

TE'06

15 min 4:55

LASER INDUCED FLUORESCENCE SPECTRUM OF THE $A^2\Pi - X^2\Sigma$ TRANSITION OF ZrN, C.M.-T. CHAN, HAIYANG LI AND A.S.-C. CHEUNG, Department of Chemistry, The University of Hong Kong, Pokfulam Road, Hong Kong.

The $A^2\Pi - X^2\Sigma$ transition of ZrN between 5631 and 5879 Å has been studied using laser induced fluorescence spectroscopy. ZrN was produced by reacting vaporized $ZrCl_4$ with microwave discharged N_2 gas. All the 12 branches of the (0,0) and (1,1) bands have been observed and assigned. Various perturbations in $v = 0$ and 1 level of the $^2\Pi$ state have been found. The magnetic hyperfine structure of the ^{91}ZrN has also been identified. Molecular constants of both the $A^2\Pi$ and $X^2\Sigma$ states of four isotopic molecules will be reported.

TE'07

10 min 5:12

Laser Absorption Spectroscopy of LaF^+ : Accurate Term Energies for the $H^2\Pi$, $D^2\Phi$, and $X^2\Delta$ States

L. A. Kaledin, A. L. Kaledin, and M. C. Heaven, *Department of Chemistry, Emory University, Atlanta, GA 30322*.

The laser absorption spectrum of the LaF^+ molecular ion has been observed for the first time. Gas phase LaF was obtained by heating a mixture of a 0.2 g of La metal and 0.3 g of LaF_3 powder to 1900 K. LaF^+ ions were produced by passing a 25 kHz discharge (80-100W, 0.5A peak current) through the vapor. Under these conditions the Tantalum heating tube used to vaporize the sample also acted as a hollow cathode. 138 lines of the $^2\Phi_{2.5} - ^2\Delta_{1.5}$ (0,0) band were recorded. This band system was observed previously ^a in the emission spectrum of LaF^+ . Accurate term energies are (in cm^{-1}):

$$T_0(H^2\Pi_{1.5}) = 30398.78(5), T_0(D^2\Phi_{3.5}) = 17099.24(5), T_0(X^2\Delta_{2.5}) = 274.62(5), \\ T_0(H^2\Pi_{0.5}) = 30237.85(5), T_0(D^2\Phi_{2.5}) = 16534.738(5), T_0(X^2\Delta_{1.5}) = 0.0$$

Ligand field theory models were used to provide the configurational assignment for the LaF^+ electronic states. The symmetry for the ground state of the LaF^+ molecular ion has been reassigned as $X^2\Delta$.

Work supported by AFOSR under grant F19628-90-C-025.

^aE. A. Shenayavskaya and L. V. Gurvich, J. Mol. Spectrosc. 81, 152-163 (1980).

TE'08

5 min 5:24

Laser Absorption Spectroscopy of LaF: Analysis of the $B^1\Pi-X^1\Sigma^+$ Transition

L. A. Kaledin, A. L. Kaledin, and M. C. Heaven, *Department of Chemistry, Emory University, Atlanta, GA 30322.*

Laser absorption spectrum of the LaF $B^1\Pi-X^1\Sigma^+$ (2,0), (1,0), (2,1), and (3,2) bands was recorded. Gas phase LaF was obtained by heating a mixture of a 0.2 g of La metal and 0.3 g of LaF₃ powder to 1900 K. In order to modulate the absorption signal, the concentration of LaF was varied by passing a 25 kHz discharge (80-100W, 0.5A peak current) through the vapor. Under these conditions the Tantalum heating tube used to vaporize the sample also acted as a hollow cathode. The B-X band system was observed previously ^a. In analyzing the spectrum, we have combined absorption data with that from the Reference. Accurate molecular constants (in cm⁻¹) and internuclear distance r_e (in nm) for the $X^1\Sigma^+$ state are:

$$\omega_e = 573.318, \omega_e x_e = 2.18, B_e = 0.246411(15), \alpha_e = 1.251(15) \times 10^{-3}, r_e = 0.20232.$$

Rotational perturbations were evident in the $B^1\Pi$ $v'=1, v'=2$, and $v'=3$ levels. The pattern of the $B^1\Pi$ state perturbations was shown to be a consequence of the interaction with the $c_1^3\Delta_1$ state by using the experimental value of $\omega_e = 450$ cm⁻¹ (see Reference) and estimated value of $\omega_e x_e = 3.5$ cm⁻¹ for the triplet state. The principal new results to emerge from this investigation are the determination of the equilibrium constants for the $B^1\Pi$ and $X^1\Sigma^+$ states of LaF.

Work supported by AFOSR under grant F19628-90-C-025.

^aH. Schall, C. Linton, and R. W. Field, *J. Mol. Spectrosc.* 100, 437-448 (1985); B. Simard and A. M. James, *J. Chem. Phys.* 97, 4669-4678 (1992)

TE'09

15 min 5:31

ELECTRONIC SPECTROSCOPY OF RuC FROM 12,000 to 19,000 cm⁻¹, I.D. LANGENBERG, R.DABELL, D.DREESSEN, AND M.D.MORSE, Department of Chemistry, University of Utah, Salt Lake City, UT 84112.

Resonant two-photon ionization spectroscopy has been applied to jet-cooled RuC, revealing transitions originating both from the $X^3\Delta$ state and from a metastable $^1\Sigma$ state. Transitions from the $X^3\Delta$ state to one $^3\Phi$, one $^3\Pi$, and two $^3\Delta$ states have been observed, along with transitions from the metastable $^1\Sigma$ state to two higher-lying $^1\Pi$ states. All of the systems have been rotationally resolved and analyzed, and several vibrational levels are known for most of the excited states. From this work a rather complete picture of the RuC electronic states lying between 1.5 and 2.5 eV has emerged. These data will be presented, along with a molecular orbital interpretation of the nature of the various states.

TF01

15 min 1:30

RENNER-TELLER CORRELATION DIAGRAMS FOR ORBITAL ANGULAR MOMENTUM IN Π AND Δ STATES OF TRIATOMIC MOLECULES

G. DUXBURY AND B. D. MCDONALD, *Department of Physics and Applied Physics, Strathclyde University, Glasgow G4 0NG, Scotland, U.K.*; A. ALIJAH, *Facultät für Chemie, Universität Bielefeld, D-4800 Bielefeld, Germany.*

A method is described for relating the energy level correlation diagrams introduced by Renner to the angular momentum "sawtooth" correlation diagrams constructed by Jungen and Merer.^a In order to do this new spin-orbit coupling versions of the diagrams are introduced for the strictly linear and bent-linear behaviour, and a version of the linear "sawtooth" diagram is constructed. Finally the effects of vibrational resonances are introduced to modify the interference effects seen in the "sawtooth" diagrams. The diagrams are constructed using an extension of the calculation method first introduced by Barrow, Dixon and Duxbury^b to allow $\langle Lz \rangle$ to be obtained.

^aMolec. Phys. 40, 1 (1980)

^bMolec. Phys. 27, 1217 (1974)

TF02

15 min 1:47

FERMI RESONANCE PERTURBATIONS OF ORBITAL ANGULAR MOMENTUM (RENNER-TELLER) COUPLING IN TRIATOMIC MOLECULES: THE STRETCH-BENDER APPROACH

G. DUXBURY AND B. D. MCDONALD, *Department of Physics and Applied Physics, Strathclyde University, Glasgow G4 0NG, Scotland, U.K.*; Ch. JUNGEN, *Laboratoire Aimée Cotton de CNRS, Université de Paris-Sud, 91405 Orsay CEDEX, FRANCE*; A. ALIJAH, *Facultät für Chemie, Universität Bielefeld, D-4800 Bielefeld, Germany.*

Fermi resonance effects on Renner-Teller coupling in NH_2 and CH_2 have been identified. We have developed an extension of the semi-rigid bender approach of Jungen and Merer^a and of Duxbury and Dixon^b to calculate the interplay between Renner-Teller and vibrational resonances in detail. The basic idea is that if in the semi-rigid bender the bond length relaxes to follow the minimum on the potential energy surface, the effect of the stretch-bend coupling should be minimised in this basis. This should simplify the calculations compared to those using a full three dimensional basis when only a few quanta of the stretching vibrations are excited via resonances. The effects of the interplay between Renner-Teller and vibrational coupling will be discussed using some of the most recent data^c obtained for the \bar{b} state of CH_2 , making use of two-dimensional wavefunctions without and with Fermi resonance effects.

^aMolec. Phys. 40, 1 (1980)

^bMolec. Phys. 43, 255 (1981)

^cB. C. Chang, M. Wu, G. E. Hall and T. J. Sears J. Chem. Phys. 101, 9236 (1994)

TF03

15 min 2:04

THE ULTRA VIOLET SPECTRUM OF THE NCN RADICAL

S. A. BEATON, J. M. BROWN, *Physical and Theoretical Chemistry Laboratory, South Parks Road, Oxford, UK, OX1 3QZ*; Y. ITO, *Department of Mechanical Engineering, Nagaoka University of Technology, 1603-1 Kamitomioka, Nagaoka, Niigata 940-21, Japan*.

The (0,0) band of the $\tilde{A}^3\Pi_u - \tilde{X}^3\Sigma_g^-$ transition of NCN, observed previously by Herzberg and Travis^a, has been reinvestigated by means of laser-induced fluorescence at 329 nm. A frequency doubled dye laser was used to record the spectrum of NCN downstream of a microwave discharge through N₂ and CF₄ in He^b. From the rotational analysis, improved values for the molecular constants of NCN in both states were obtained, including Λ -type doubling parameters for the $^3\Pi_u$ upper state.

The main molecular constants obtained were

$$\begin{aligned}\tilde{X}^3\Sigma_g^-: \quad B''_{000} &= 0.3972458(95)\text{cm}^{-1} \quad \lambda'' = 0.79402(50)\text{cm}^{-1} \\ \tilde{A}^3\Pi_u: \quad B'_{000} &= 0.3966487(95)\text{cm}^{-1} \quad A' = -37.4493(38)\text{cm}^{-1} \\ T'_{000} &= 30383.8110(51)\text{cm}^{-1}\end{aligned}$$

The B values (and hence bond lengths) are very similar in the two states and therefore the spectrum is dominated by $\Delta v = 0$ transitions.

The (010)-(010) band occurs in a similar wavelength region, the excited state of this transition exhibiting the Renner-Teller effect. Analyses of both the $^3\Delta_g - ^3\Pi_u$ and the $^3\Sigma_g - ^3\Pi_u$ components of this hot band will be presented.

^aG.HERZBERG AND D.N.TRAVIS, *Can.J.Phys.* **42**,1658-1675 (1964).

^bG.P.SMITH, R.A.COPELAND AND D.R.CROSLEY, *J.Chem.Phys.* **91**,1987-1993 (1989).

TF04

15 min 2:21

HIGH RESOLUTION LIF SPECTROSCOPY OF THE MgNC RADICAL.

ROSSANA RUBINO, CHRISTOPHER C. CARTER, JAMES M. WILLIAMSON, DAVID E. POWERS AND TERRY A. MILLER., *Laser Spectroscopy Facility, Department of Chemistry, The Ohio State University, Columbus, OH 43210*.

High resolution, rotationally resolved, laser induced fluorescence spectra for the origin band as well as several transitions involving vibrationally excited levels of MgNC have been recorded. MgNC free radicals were generated in a supersonic free jet expansion by simultaneous laser ablation of magnesium and photolysis of acetonitrile. The radicals were probed by a pulse-amplified Ti:Sapphire ring dye laser. Rotational analysis yields both the ground and excited state molecular constants for the studied vibronic transitions. The ground state rotational constants are in good agreement with previous microwave studies of MgNC, which gives additional support for the identification of the carrier of the spectra. Vibronic assignments of these bands, which are consistent with the rotational analysis, will be discussed.

TF05

15 min 2:38

Optical Spectroscopy of the Niobium Methylidyne Free Radical, NbCH

David A. Gillett, M. Barnes, G.F. Metha^a, K. Athanassenas and A.J. Merer, *Department of Chemistry, University of British Columbia, 2036 Main Mall, Vancouver, B.C. V6T 1Z1, Canada.*

Pulsed laser excitation spectra of niobium methylidyne (NbCH) have revealed 29 bands for NbCH and 17 for NbCD in the wavelength region 545–625 nm. NbCH was produced in a supersonic free jet expansion in helium by reacting methane with laser ablated niobium (355 nm Nd:YAG).

The band structure can be organised into transitions involving excitation from the $\tilde{X}^3\Delta_1$ ground state to numerous vibronic levels of two close lying excited electronic states with $\Omega=2$ and $\Omega=1$, whose origins are near 16050 cm^{-1} and 16250 cm^{-1} respectively. Upper state assignments are complicated by a large vibronic (Renner-Teller) coupling between the two states and random perturbations due to 'dark' states.

Wavelength resolved fluorescence spectra of NbCH(NbCD) have allowed us to determine two of the three \tilde{X} state vibrational fundamentals:

$$\nu_2 = 603(466)\text{ cm}^{-1}, \nu_3 = 905(858)\text{ cm}^{-1}.$$

Work is currently underway to record the (0,0) bands at cw laser resolution, which will allow accurate structural parameters to be determined and will resolve the niobium nuclear hyperfine structure. Modelling of the Renner-Teller interaction between the vibronic levels of the two close lying excited electronic states is also in progress.

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TF06

15 min 2:55

THE ELECTRONIC SPECTRUM OF TANTALUM METHYLIDYNE, TaCH

M. BARNES, DAVID A. GILLETT, G. F. METHA^a, K. ATHANASSENAS and A.J. MERER, *Department of Chemistry, University of British Columbia, 2036 Main Mall, Vancouver, B.C. V6T 1Z1, Canada.*

Tantalum methylidyne, TaCH, has been produced in a supersonic free jet expansion in helium by the reaction between laser ablated tantalum and methane. TaCD has been made similarly using CD₄.

Pulsed dye laser excitation spectra from the $\Omega=0^+(\tilde{X}^1\Sigma^+)$ state of TaCH have been assigned to two electronic transitions whose upper states have $\Omega=0^+$, which probably is $^3\Pi$, and $\Omega=1$. The (0,0) bands of these states lie at 15638.6 cm^{-1} and 16398.3 cm^{-1} , respectively.

Wavelength resolved fluorescence emission from the $\Omega=0^+$ excited state has revealed a low lying $\Omega=1$ electronic state 3620 cm^{-1} above the ground state; this appears to be a $^3\Delta_1$ state. Two of the \tilde{X} state vibrational fundamentals have been determined for TaCH(TaCD): $\nu_2 = 641(492)\text{ cm}^{-1}$ and $\nu_3 = 955(910)\text{ cm}^{-1}$. The values determined for the $a^3\Delta_1$ state were $\nu_2 = 606(449)\text{ cm}^{-1}$ and $\nu_3 = 925(864)\text{ cm}^{-1}$.

High resolution spectra are being recorded for selected bands; these will allow the molecular structure and the spectroscopic parameters to be determined accurately. The magnetic and quadrupolar hyperfine structure of ^{181}Ta is fully resolved in the high resolution study.

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TF07

15 min 3:12

A Molecular Beam Optical Study of YCC

J. Xin, A. J. Marr and T. C. Steimle, *Department of Chemistry and Biochemistry, Arizona State University, Tempe, AZ, 85287-1604.*

A weak signal near 13395 cm^{-1} in the low resolution laser induced fluorescence spectra of the laser ablated Y/ethylene supersonic expansion products was noted by Simard^a. He speculated that it may be due to yttrium dicarbide. Following up on his suggestion, we have detected by medium resolution LIF three red degraded bands at 12895 cm^{-1} , 13395 cm^{-1} and 13896 cm^{-1} which we attribute to YCC. The resolved LIF spectra for the 12895 cm^{-1} and 13395 cm^{-1} band systems produce strong Stokes progressions with the features separated by approximately 560 cm^{-1} . These are tentatively assigned to the Y-CC ground state stretching. Additional weaker features are also observed. The high resolution LIF spectrum of the 12895 cm^{-1} band system was recorded. Attempts to model the spectrum as a $\tilde{A}^4\text{ A}_1\text{-}\tilde{X}^2\text{ A}_1$ transition suggested by a recent ab initio calculation^b are being made. Progress on the analysis will be presented.

^aBenoit Simard, Steacie Institute-NRC, Ottawa Ontario, Canada, Private Communication.

^bS. Roszak and K. Balasubramanian, *Chem. Phys. Lett.* **246**, 20 (1995).

TF08

15 min 3:29

THE OPTICAL AND OPTICAL/STARK SPECTRUM OF IRIIDIUM MONOCARBIDE AND MONONITRIDE

A. J. MARR, M. E. FLORES and T. C. STEIMLE, *Dept. of Chemistry and Biochemistry, Arizona State University, Tempe, AZ 85287-1604.*

Supersonic molecular beam samples of iridium monocarbide, IrC, and iridium mononitride, IrN, were generated using a laser ablation/reaction source and characterized using high resolution ($\Delta\nu < 30\text{ MHz FWHM}$) laser induced fluorescence spectroscopy. This is the first identification of gaseous IrN. The conventional high temperature spectra of IrC was recorded some time ago^{a,b}. Numerous strong band systems in the 18800 cm^{-1} to 14360 cm^{-1} spectral range were assigned as the $(v',0)$ progression of the $\tilde{A}^1\Pi - \tilde{X}^1\Sigma^+$ band system of IrN. The (1,0) and (0,0) bands were analyzed to produce a set of fine and hyperfine parameters. The electric field induced effects on the $R(0)$ branch features of these bands were analyzed to produce permanent electric dipole moments: $\tilde{A}^1\Pi(v=0)$ 2.78(2) D, $\tilde{A}^1\Pi(v=1)$ 2.64(2) D and $\tilde{X}^1\Sigma^+(v=0)$ 1.66(1) D. The (0,0) $\tilde{D}^2\Phi_{7/2}\text{-}\tilde{X}^2\Delta_{5/2}$ band system of IrC was recorded and analyzed to produce a set of fine and hyperfine parameters. The electric field induced effects on the $R(2.5)$ branch feature were analyzed to produce permanent electric dipole moments: $\tilde{D}^2\Phi_{7/2}(v=0)$ 2.61(6) D and $\tilde{X}^2\Delta_{5/2}(v=0)$ 1.60(7) D. Plausible electronic configurations consistent with the experimental observations are given.

^aK. Jansson, R. Scullman and B. Yttermo, *Chem. Phys. Lett.* **4**, 188 (1969).

^bK. Jansson and R. Scullman, *J. Mol. Spectrosc.* **36**, 248 (1970).

Intermission

TF09**15 min 4:00****A New Discharge Nozzle for Spectroscopic Studies in Supersonic Jets**

Andrew J. Bezzant, Daniel D. Turner, Guy Dormer, and Andrew M. Ellis, *Department of Chemistry, University of Leicester, University Road, Leicester LE1 7RH, UK.*

We will describe a new nozzle for spectroscopic studies of reactive species in pulsed supersonic jets. This nozzle was designed as a cheap alternative to laser ablation methods for producing metal-containing species. It employs an electrical discharge to produce metal atoms by argon ion sputtering at the cathode. These metal atoms can then be mixed with the appropriate reagents to produce metal-containing species before expansion into vacuum. To avoid rapid carbon deposition onto the metal source electrode when carbon-containing reagents are used, the reactive precursor must be kept away from the metal-sputtering region. Consequently, a dual channel nozzle has been developed in which two pulsed gas sources are mixed at a common point prior to expansion. This has been extensively tested by preparing a number of spectroscopically well-characterised metal-containing species, including PtC, CdCH₃, and ZnC₅H₅.

TF10**15 min 4:17**

SPECTROSCOPY AND EXCITED STATE DYNAMICS OF BORON ATOM-RARE GAS AND B-H₂ VAN DER WAALS COMPLEXES, XIN YANG AND PAUL J. DAGDIGIAN, Department of Chemistry, The Johns Hopkins University, Baltimore, MD 21218-2685.

Laser fluorescence excitation spectra of the BNe, BAr, and B-H₂ van der Waals complexes, in the vicinity of the B atomic $2s2p^2\ ^2D \leftarrow 2s2p\ ^2P$ transition at 208.9 nm, will be reported. For BNe, partially rotationally resolved bands of the $C^2\Delta - X^2\Pi_{1/2}$ and $D^2\Pi - X^2\Pi_{1/2}$ transitions, and unstructured excitation in the dissociation continuum to the blue, were observed. For BAr, fluorescence excitation was observed only for the $D^2\Pi - X^2\Pi_{1/2}$ transition, while no B-H₂ fluorescence could be detected in this wavelength range. To detect the non-fluorescing states, fluorescence depletion experiments were carried out. With this technique, the BAr $C^2\Delta - X^2\Pi_{1/2}$ transition, and electronic transitions in the B-H₂ complex, were observed. The BAr($C^2\Delta$) and B-H₂* apparently decay by predissociation and chemical reaction, respectively. The contrasting decay behavior of the excited states of BNe, BAr, and B-H₂ will be discussed in terms of our knowledge of electronic states of these complexes. Estimated binding energies of the BNe and BAr states will be presented.

TF11**15 min 4:34****VIBRATIONAL SPECTROSCOPY OF Rg•SH COMPLEXES**

CHRISTOPHER C. CARTER, MIN-CHIEH YANG, TERRY A. MILLER, *The Ohio State University, Department of Chemistry, The Laser Spectroscopy Facility, 120 West 18th Ave., Columbus, OH 43210.*

The rotationally resolved spectra of the Rg•SH (Rg= Ne, Ar, Kr) complexes has been presented previously and is now fairly well understood. At the same time there has been considerable uncertainty in the absolute vibrational quantum numbers of these bands. In this talk we will present results of both high (~250 MHz) and moderate resolution (~0.1 cm⁻¹) laser induced fluorescence spectra. Using the isotopic shifts of ³⁴S-³²S and ⁸⁶Kr-⁸⁴Kr, we will make arguments for the absolute vibrational numbering in the various progressions of these complexes.

With this numbering we can then determine ω_e and $\omega_e x_e$ for the progressions and therefore also determine approximate D_0 and D_0' values for these complexes assuming a Morse potential.

TF12

15 min 4:51

ELECTRONIC PREDISSOCIATION DYNAMICS OF CN(A)-Ne

W. G. LAWRENCE AND M. C. HEAVEN, *Department of Chemistry, Emory University, Atlanta, GA 30322.*

The electronic predissociation process $\text{CN}(A \ ^2\Pi_{3/2}, v=3)\text{-Ne} \rightarrow \text{CN}(X, v=7) + \text{Ne}$ was characterized using sequential pulse $B \leftarrow A \leftarrow X$ excitation of the complex. Pump and probe lasers were fixed on specific complex features, and the intensity of the OODR fluorescence signal was monitored as a function of the delay between the laser pulses. Single exponential fits to these data yielded lifetimes in the range of 100-170 ns for A state rotational levels in the range $1/2 \leq J \leq 9/2$. Radiative decay occurs with a lifetime of $\approx 6 \mu\text{s}$, and makes a negligible contribution to the decay of the CN(A)-Ne levels examined. Within the experimental error limits, the predissociation rates were linearly dependent on $J(J+1)$. This behavior is characteristic of a mechanism that involves Coriolis coupling. However, the decay rate does not approach the radiative rate at the hypothetical $J=0$ limit, and it is clear that the dominant predissociation channel does not depend on Coriolis coupling. Extrapolation of the decay rate yields a lifetime of 175 ns for the non-rotating complex. This value is comparable to the lifetime of 91 ns reporting for CN(A, $v=3$) isolated in solid Ne matrix. Experimental details and a theoretical analysis of the predissociation mechanism will be presented.

TF13

15 min 5:08

AXIS SWITCHING IN THE $\tilde{B} \ ^2A' - \tilde{X} \ ^2A'$ TRANSITION OF HCO AND FLUORESCENCE LIFETIMES OF THE $\tilde{B} \ ^2A'(0,0,0)$ ROTATIONAL STATES, SHIH-HUANG LEE AND I-CHIA CHEN, *Department of Chemistry, National Tsing Hua University, Hsinchu, Taiwan 30043, Republic of China.*

Fluorescence spectra of the $\tilde{B} \ ^2A' - \tilde{X} \ ^2A'(0,0)$ band of thermalized HCO at 298 K were recorded. The lifetimes of nascent HCO $\tilde{B} \ ^2A'(0,0,0)$ states produced from acetaldehyde photolyzed at a wavelength of 310.9 nm in a supersonic jet were obtained for rotational states to $N = 26, 24$ and 18 for $K_a = 0, 1$ and 2, respectively. These states have lifetimes decrease as the K and N quantum numbers increase. The measured lifetimes vary in the ranges 24-89 ns for $K_a = 0$ states, 12-52 ns for $K_a = 1$ states and 14-18 ns for $K_a = 2$ states. An α -type Coriolis interaction between the $\tilde{B} \ ^2A'$ and $\tilde{A} \ ^2A'$ states is proposed to be the major mechanism to account for predissociation of the low vibrational levels of $\tilde{B} \ ^2A'$. The spectral intensity shows anomalous behavior in that the intensity ratio of transitions $\mathcal{Q}_{R_0}/\mathcal{Q}_{P_0}$ is nearly 2; similar phenomena are observed for other branches. The mechanism of axis switching in the $\tilde{B} \ ^2A' - \tilde{X} \ ^2A'$ transition, i.e. the geometry change during the excitation, accounts for the intensity anomaly. Corrections for the lifetime variation and intensity anomaly are necessary to obtain accurate relative populations of the $\tilde{X} \ ^2A'$ state from fluorescence spectra $\tilde{B} \ ^2A' - \tilde{X} \ ^2A'$.

TF14

10 min 5:25

ROTATIONALLY RESOLVED LIF SPECTRA OF JET-COOLED HCCS RADICAL

JAMES M. WILLIAMSON, CHRISTOPHER C. CARTER, DAVID E. POWERS, ROSSANA RUBINO, AND TERRY A. MILLER, *The Ohio State University, Department of Chemistry, The Laser Spectroscopy Facility, 120 West 18th Ave., Columbus, OH 43210.*

We have obtained the high resolution, rotationally resolved LIF spectra of the electronic origin and several excited vibrational bands near 24660 cm^{-1} of the HCCS radical. The HCCS was produced by the low powered KrF laser photolysis of thiophene in a free-jet expansion. The LIF spectra was obtained by a pulse-amplified, Ti:Sapphire ring-dye laser with a resolution of $\sim 250\text{ MHz}$. The rotational analysis of the origin band agrees well with microwave data for the ground electronic state. This paper will present the LIF spectra and the rotational analysis of all the bands will be discussed.

TF15

10 min 5:37

ROTATIONALLY RESOLVED NEAR-INFRARED SPECTRUM OF HCB_r, BOR-CHEN CHANG AND TREVOR J. SEARS, Department of Chemistry, Brookhaven National Laboratory, Upton, New York 119730-5000.

The rotationally resolved spectrum of bromomethylene (HCB_r) in the vicinity of 12800 cm^{-1} was obtained at Doppler-limited resolution using a transient frequency-modulation absorption technique. In contrast to the better studied halo-methylenes (HCF and HCCl), the number of experimental investigations on HCB_r is very limited. Xu *et al.*^a reported the $\tilde{A} \leftarrow \tilde{X}$ spectrum at visible wavelengths, but no rotational structure was resolved. Gilles *et al.*^b have used photoelectron spectroscopy to determined the singlet-triplet separation to be $2.6 \pm 2.2\text{ kcal/mol}$. Based upon previous studies^{a,b}, we tentatively assign the observed band to be the $\tilde{A}^1A''(0,2,0) \leftarrow \tilde{X}^1A'(0,0,0)$ transition. The analysis of the observed spectrum will be discussed.

Acknowledgment: This work was carried out under Contract No. DE-AC02-76CH00016 with the U.S. Department of Energy and supported by its Division of Chemical Sciences, Office of Basic Energy Sciences.

^aS. Xu, K. A. Beran, and M. D. Harmony, *J. Phys. Chem.* **98**, 2742 (1994).

^bM. K. Gilles, K. M. Ervin, J. Ho, and W. C. Lineberger, *J. Phys. Chem.* **96**, 1130 (1992).

TF16

10 min 5:49

THE PRODUCTION OF RADICAL SPECIES BY A HIGH TEMPERATURE NOZZLE IN A FREE JET EXPANSION: THE STUDY OF CF₂ AND CFB_r BY LASER INDUCED FLUORESCENCE

Melanie R. Cameron, Pamela. T. Knepp and Scott. H. Kable, *Department of Physical Chemistry, University of Sydney, Sydney, NSW, AUSTRALIA, 2006.*

A simple design for a heated nozzle, having the capability of reaching approximately 1200K will be presented. This nozzle, in conjunction with a free jet experimental apparatus, has been used to produce radical species which are subsequently probed by the technique of fluorescence excitation spectroscopy.

The discussion will focus on two particular radical species, CF₂ and CFB_r. For CF₂, the rotationally resolved first excited state fluorescence lifetimes will be addressed. The CFB_r radical has been utilized as a precursor in the dynamical study of the photodissociation reaction producing CF and Br.

TG01

15 min 1:30

RESONANT ION DIP INFRARED SPECTROSCOPY (RIDIRS) OF BENZENE-(METHANOL)_m HYDROGEN-BONDED CLUSTERS

R. N. PRIBBLE, F. C. HAGEMASTER, AND T. S. ZWIER, *Department of Chemistry, Purdue University, West Lafayette, IN 47907-1393.*

Infrared spectra of benzene-(methanol)_m clusters formed in a jet-cooled molecular beam are recorded in the methanol ν_1 O-H stretch region (3100 to 3800 cm^{-1}). RIDIRS utilizes Resonant 2-Photon Ionization Time-of-Flight Mass Spectroscopy (R2PI-TOFMS) to monitor a size selected cluster's ion signal which is proportional to its neutral ground state population. The tunable infrared output of a Nd:YAG-pumped OPO system is spatially overlapped with the R2PI near-UV pulsed laser beam and precedes it by 80 ns. When in resonance with an infrared transition, population is removed from the cluster's neutral ground state prior to ionization, producing a dip in the R2PI ion signal. Experimental hydrogen-bond vibrational signatures (i.e. vibrational frequency shifts and changes in band widths), along with ab initio calculations, provide structural information about each cluster. Chain structures exist for benzene-(methanol)₁₋₃, and methanol cyclic structures are attached to benzene in benzene-(methanol)₄₋₆.

TG02

15 min 1:47

ROTATIONALLY RESOLVED VIBRATIONAL OVERTONE SPECTRA OF JET-COOLED METHANOL

OLEG V. BOYARKIN, LUCIA LUBICH, THOMAS R. RIZZO, *Laboratoire de chimie physique moléculaire, Ecole Polytechnique Fédérale de Lausanne, CH- Ecublens, 1015 Lausanne, Switzerland;* and
DAVID S. PERRY, *Department of Chemistry, University of Akron, Akron, Ohio, 44325.*

Infrared-optical double resonance excitation permits the measurement of fully rotationally resolved vibrational overtone spectra of jet-cooled methanol up to the $6\nu_{OH}$ level. These weak transitions to high vibrational levels are detected using the technique of IR assisted photofragment spectroscopy (IRLAPS). The elimination of spectral congestion reveals splittings of the zeroth-order rovibrational levels that reflect vibrational coupling to dark background levels. Analysis of the overtone spectra as a function of the number of OH stretch quanta indicates the presence of a strong coupling between zeroth-order states with $n\nu_{OH}$ and those with $(n-1)\nu_{OH} + \nu_{CH_{asym.st.}}$. This coupling is most clearly manifest at the $5\nu_{OH}$ level where the OH stretch frequency is anharmonically shifted close to that of the CH asymmetric stretch frequency. Finer spectral splittings reflect the coupling of the mixed OH-CH stretch states with the rest of the vibrational bath. The most recent results using this technique for CH_3OH and its partially deuterated analogs will be discussed.

TG03

15 min 2:04

JET-COOLED INFRARED SPECTRA AND INVESTIGATION OF THE TORSION-ROTATION ENERGY LEVELS OF METHANOL IN THE C-H STRETCH REGION, LI-HONG XU, Department of Physical Sciences, University of New Brunswick, Saint John, N.B., Canada E2L 4L5; X. WANG and D.S. PERRY, Department of Chemistry, University of Akron, Akron, OH 44325-3601; G.T. FRASER AND A.S. PINE, Radiometric Physics Division, National Institute of Standards and Technology, Gaithersburg, MD 20899.

Jet-cooled absorption spectra of the C-H stretching bands of methanol have been recorded between 2965 and 3027 cm^{-1} on two different molecular beam machines. In both cases, a color-center laser pumped by ~ 1.6 W from a krypton ion laser at 647 nm was used to generate 8-9 mW of tunable IR radiation. The first spectrum between 2977-3027 cm^{-1} was recorded in direct absorption with a 2×0.01 cm slit nozzle. The molecular rotational temperature was ~ 17 K, and the linewidth was ~ 75 MHz due to residual Doppler spread. Baseline subtraction was employed to suppress laser intensity fluctuations. Frequency calibration was accomplished by simultaneously recording absorption lines of ethylene and the transmission fringes of a vacuum-spaced 150 MHz-marker etalon. The second spectrum between 2965-3027 cm^{-1} was recorded on a molecular-beam optothermal spectrometer. A mixture of a few percent methanol in He carrier was introduced to the beam chamber through a 60- μm pinhole nozzle with ~ 1 atm backing pressure, giving a rotational temperature of ~ 10 K. The beam was focused onto a He-cooled bolometer using quadrupole focusing in the flight chamber between the skimmer and the detector. In a few pathological regions, H_2O absorption completely obscured the methanol spectrum and spoiled control of the laser scan. Calibration traces were recorded to minimize errors due to gaps and drifts. On a given day the calibration interferometer drift was typically less than ~ 10 MHz, defining the overall precision. Separations of close lines in a single scan should have precision better than 1 MHz. The two spectra were combined for analysis, with the straight absorption spectrum giving particularly nice and easily recognizable spectral patterns.

Line assignments were initially made by MW-IR double resonance, pattern recognition, and fits of individual subbands to polynomials in m ($m = J + 1$, J , and $-J$ for R -, Q -, and P -branch transitions, respectively). They were checked with stringent combination loop tests. About 20 subbands have been confirmed up to $K'_{\text{max}} = 3$ for A and E torsional symmetries respectively, all for the $\nu_2 A'$ asymmetric C-H stretching fundamental. (The vibrational identification is based on literature information.) For several subbands, perturbations were identified along with associated satellite components. Torsion- K -rotation energies were deduced for the excited vibrational state by adding the experimental IR subband origins to calculated ground state energies. The A/E torsional energy pattern is found to be reversed compared to the ground state, as seen for other methanol fundamentals and other molecules. For the systems with identified perturbations, off-diagonal interaction matrix elements have been determined, and attempts to fit the observed excited-state energy pattern are in progress.

TG04

10 min 2:21

JET-COOLED INFRARED SPECTRUM OF THE ν_6 BAND OF CH_2F_2

THOMAS J. CRONIN, XIAOLIANG WANG, AND DAVID S. PERRY, *Department of Chemistry, The University of Akron, Akron, OH 44325-3601*; GREGORY A. BETHARDY, *Chemistry Division, Argonne National Laboratory, Argonne, IL 60439*.

A high resolution infrared spectrum of the asymmetric C-H stretching band ν_6 was recorded between 3003 - 3035 cm^{-1} using a slit-jet absorption apparatus. The dataset contains 500 lines including 10 sub-bands of the ν_6 band and 5 sub-bands of the $2\nu_2$ overtone. Analysis and spectroscopic constants will be reported.

TG05

15 min 2:33

MBER SPECTROSCOPY OF ISOCYANIC ACID (HNCO)

BRIAN MEEHAN, and J. S. MUENTER, *Department of Chemistry, University of Rochester, Rochester, NY 14627*.

Recent studies of vibrationally mediated photodissociation of HNCO ^a point to the need for better understanding of the vibrational dependence of HNCO electronic properties. A necessary preliminary to excited state measurements is accurate characterization of ground state properties. The present work describes molecular beam electric resonance studies of several rotational levels in the ground vibrational state of isocyanic acid. Dipole moment and hyperfine results will be presented.

^aS. S. Brown, H. L. Berghout, and F. F. Crim, *J. Chem. Phys.* 102, 8440 (1995).

TG06**15 min 2:50****THE MICROWAVE SPECTRUM OF A MOLECULAR EIGENSTATE I**BROOKS H. PATE, *Department of Chemistry, University of Virginia, Charlottesville, VA 22901.*

When a molecule is excited to a region of high state density, the rovibrational spectrum becomes much more complicated due to the intramolecular vibrational energy redistribution process (IVR). The single rovibrational transition expected in the harmonic normal mode approximation appears as a set of transitions forming the IVR multiplet. Each transition corresponds to a different eigenstate of the full molecular Hamiltonian. The molecular eigenstates are superpositions of the coupled normal mode vibrational basis states. The rotational spectrum of a single eigenstate is discussed. Even when only anharmonic coupling is present, the microwave spectrum of the eigenstate contains a series of transitions. This result reflects the fact that a molecular eigenstate at one value of J is not an eigenstate at a different value, such as $J+1$, because of the vibration-rotation terms usually incorporated in the vibrational dependence of the rotational constant. The dynamics following coherent excitation from a single eigenstate are further complicated by the vibrational dependence of the molecular dipole moment. The effects of these terms, and also the effects of the anharmonic coupling strength, are investigated to determine the appearance of the high resolution spectrum and the nature of the coherent state produced by broad band excitation.

TG07**15 min 3:07****THE MICROWAVE SPECTRUM OF A MOLECULAR EIGENSTATE II**BROOKS H. PATE, CHUNG YI LEE, *Department of Chemistry, University of Virginia, Charlottesville, VA 22901.*

Experimental infrared-microwave double-resonance techniques for measuring the microwave spectrum from a single molecular eigenstate are presented. The most difficult requirement for a general technique to study this problem is that the double-resonance technique must work in the absence of saturation of the infrared transition. We have developed a molecular beam double-resonance technique, based on the Autler-Townes splitting of the molecular eigenstate when it is subjected to a strong, resonant microwave field, that meets this requirement. This technique allows us to measure the microwave transition frequencies for the eigenstate along with the transition strength. In some cases, an infrared-microwave-microwave triple-resonance technique can be used which provides an enhanced sensitivity. Using the triple-resonance method, transitions as weak as 0.015D can be measured. The results of measurements on single eigenstates of propargyl alcohol are discussed with relation to the theory presented in the previous paper.

Intermission

TG08

15 min 3:40

EIGENSTATE RESOLVED INFRARED SPECTROSCOPY OF 1,1,1-d₃-ETHANE IN THE REGION AROUND 5900 CM⁻¹

J. W. DOLCE, A. CALLEGARI, H. K. SRIVASTAVA, K. K. LEHMANN, and G. SCOLES, *Princeton University, Department of Chemistry, Princeton, NJ, 08544.*

This talk will describe results which are part of a series of experiments studying intramolecular vibrational energy redistribution (IVR) in medium size molecules containing a methyl group. Last year we reported on methylsilane^a, while this year we will discuss the results for 1,1,1-d₃-ethane also obtained using optothermal detection, cavity enhanced, molecular beam laser spectroscopy. A 9 cm⁻¹ wide section in the 5900 cm⁻¹ C-H stretch overtone region was observed. All molecules we have studied with an axial methyl group have a strong parallel band in this region with band origins within a few cm⁻¹ of each other. We believe the best zero order assignment for these bands is as the first overtone of the asymmetric methyl CH stretch. For the CH₃CD₃ band, Lawrence-Knight deconvolution of the rotationally assigned transitions reveals that the coupling strengths of this state to the nearly isoenergetic background of vibrational states range from 1×10^{-3} to 25×10^{-3} cm⁻¹. The observed coupling strengths do not show a systematic dependence from the rotational quantum number for the low J,K values that we have observed in our beam experiment, and therefore appear to be dominated by anharmonic forces. These results will be discussed in light of those previously obtained for methylsilane and other similar molecules.

^aTalk RK11, 1995.

TG09

15 min 3:57

EIGENSTATE RESOLVED INFRARED AND MILLIMETER WAVE - INFRARED DOUBLE RESONANCE STUDY OF METHYLAMINE IN THE N-H STRETCH OVERTONE REGION

H. K. SRIVASTAVA, A. CALLEGARI, K. K. LEHMANN, G. SCOLES, *Princeton University, Department of Chemistry, Princeton, NJ, 08544*; U. MERKER^a, *University of Bonn, Institut für Angewandte Physik, Wegelerstr. 8, 53115 Bonn, Germany.*

The infrared spectrum of methylamine, CH₃NH₂, was recorded in the region of the $\nu_1 + \nu_{10}$ N-H stretching overtone (6600 cm⁻¹), using a molecular beam laser spectrometer with optothermal detection. This molecule is an interesting benchmark for the study of intramolecular vibrational energy redistribution (IVR) because of its two large amplitude internal motions: CH₃ rotation and NH₂ wagging that are coupled together. However this also makes assigning the spectrum a challenge due to its extreme congestion. The single photon spectrum yields a density of approximately 1000 lines/cm⁻¹. Millimeter wave-infrared double resonance has been used to isolate the contributions from a single ground state. Preliminary inspection of the double resonance spectrum suggests that the IVR rates are faster than those observed for molecules of comparable structure and size.^b Analysis of the data is in progress, and further results will be presented at the conference.

^aSupported by the German Academic Exchange Service (DAAD)

^bTalk RK11, 1995.

TG10

15 min 4:14

EIGENSTATE RESOLVED INFRARED AND INFRARED-INFRARED DOUBLE RESONANCE STUDY OF BENZENE VIBRATIONAL RELAXATION IN THE C-H STRETCH FIRST OVERTONE REGION

A. CALLEGARI, H. K. SRIVASTAVA, K. K. LEHMANN, G. SCOLES, *Princeton University, Department of Chemistry, Princeton, NJ, 08544*; U. MERKER^a, *University of Bonn, Institut für Angewandte Physik, Wegelerstr. 8, 53115 Bonn, Germany*.

The eigenstate resolved, infrared spectrum of benzene, C₆H₆, was recorded in the region of the first C-H stretching overtone (6000 cm⁻¹). The spectrum was observed using a molecular beam laser spectrometer with optothermal detection. The Benzene overtone spectrum has long been one of the most important model systems for studies of Intramolecular Vibrational energy Relaxation (IVR), and has been the subject of numerous experimental and theoretical investigations. The best previous investigation of the first CH overtone region gave an effective resolution of 4 cm⁻¹ due to the convolution of laser linewidth and rotational structure. By using our spectrometer, with an instrumental resolution of ~ 5 MHz (~ 2 × 10⁴ times higher than the previous study), we have observed an extremely dense spectrum, with a density of thousands of lines per cm⁻¹. Given the density of the spectrum, combined with the highly 'degenerate' rotational structure expected for a perpendicular transition in a planar symmetric top, rotational assignment by combination differences appeared unpromising. In order to make progress with the analysis of the spectrum, we have exploited near coincidences of the Q(2,0) and Q(3,0) transitions of the benzene ν₁₄ fundamental with the R₃₀ line of the ¹³CO₂ laser. This allowed us to use mid-IR/near-IR double resonance to observe the spectrum of a single lower rotational state by modulation of the CO₂ radiation (which crossed the molecular beam before the near-IR radiation), while scanning the near-IR laser. To date, we have observed the spectrum near the strongest transition (6006 cm⁻¹) observed in the previous study. We observe three 'clumps' of lines whose centers are separated by the expected P, Q, and R transitions from the J=2 lower state. The clumps have full width of ~ 0.5 cm⁻¹, implying an IVR lifetime for this 'feature state' of ~ 10 ps. The clumps, however, reveal sub-structure, which implies the presence of dynamical bottle-necks to IVR on even longer timescales. Analysis of the data is in progress.

^aSupported by the German Academic Exchange Service (DAAD)

TG11

10 min 4:31

MOLECULAR BEAM INFRARED SPECTRUM OF THE FIRST C-H STRETCHING OVERTONE REGION OF NITROMETHANE

M. HALONEN^a, L. HALONEN^a, K. K. LEHMANN AND A. CALLEGARI, *Department of Chemistry, Princeton University, NJ 08544*.

The first C-H stretching overtone region of nitromethane has been measured using a bolometer detected molecular beam machine with a resonance cavity. Nitromethane is an almost free rotor with a very low torsional barrier in the ground state. The purpose of this study is to find out whether the low 6-fold barrier of the ground state will turn to a much higher 2-fold barrier in the first stretching vibrational overtone of nitromethane with 2 quanta of stretching vibrational energy.^b This might happen, if the vibrational energy would stay localised in one bond long enough compared with the period of internal rotation.

The spectrum of nitromethane has been measured in the wavenumber region 6047-6055 cm⁻¹ with a resolution of 5MHz. As the rotational temperature is very low, only levels with the internal rotation quantum number m=0 and m=1 should be significantly populated. The spectrum has been assigned using ground state combination differences. Using a rigid rotor program the band center and the rotational constants have been obtained for the m=0 state. The analysis of the m=1 state is in progress.

^aPermanent address of M. and L. Halonen: Laboratory of Physical Chemistry, P.O. Box 55 (A.I. Virtasen aukio 1), FIN-00014 University of Helsinki, Finland

^bD. Cavagnat, L. Lespade, and C. Lapouge, Ber. Bunsenges. Phys. Chem. 99, 544 (1995)

TG12

5 min 4:43

INFRARED SPECTRA OF METHYLAMINE IN THE ASYMMETRIC C-H STRETCH REGION

ANDREI V. CHIROKOLAVA, THOMAS J. CRONIN, XIAOLIANG WANG, C. MICHAEL LINDSAY, AND DAVID S. PERRY, *Department of Chemistry, The University of Akron, Akron, OH 44325-3601.*

High-resolution IR spectra of methylamine were obtained using slit jet absorption spectroscopy. A total of 1330 lines were recorded in the asymmetric C-H stretch region ($2965\text{--}3005\text{ cm}^{-1}$). Hindered internal rotation about the C-N bond and inversion of amino group complicate the analysis of the observed spectra. The subbands are found by fitting the lines to quartic polynomials and these assignments are confirmed by comparison with ground state combination differences based on microwave and far infrared data.

TG13

15 min 4:50

INFRARED DIODE-LASER MOLECULAR BEAM SPECTRUM OF THE ν_2 BAND OF ClONO_2 AT 1293 cm^{-1} , J.L. DOMENECH, Instituto de Estructura de la Materia, CSIC, Serrano 119, 28006 Madrid, Spain, I.-M. FLAUD, LPMA, Université P. et M. Curie, 4, Place Jussieu 75252 Paris Cedex 05, France, G.T. FRASER, A.M. ANDREWS, W.J. LAFFERTY, Optical Technology Division, NIST, Gaithersburg, MD 20899 and P.L. WATSON, Dupont Central Research and Development, Experimental Station E328/314, P.O. Box 80328, Wilmington, DE 19880-0328.

A diode-laser spectrometer has been used to obtain the IR spectrum of the ν_2 band of chlorine nitrate which was prepared by the reaction of ClF with dry nitric acid. Observed line widths range between 65 to 90 MHz, mainly due to laser jitter. The effective rotational temperature obtained was about 23 K and the spectrum was completely resolved with the exception of a-type Q-branches at the band center. The P- and R-branch lines of both the ^{35}Cl and ^{37}Cl isotopic species have been completely assigned, and a complete set of spectroscopic constants has been derived for both isotopomers. Attempts to model the band contour at stratospheric temperatures will be discussed.

TG14

15 min 5:07

The $\nu_7 + \nu_9 - \nu_9$ Hot Band in Ethane

W. Leo Meerts, Jos Oomens, Jörg Reuss, *Department of Molecular and Laser Physics, Catholic University of Nijmegen, Toernooiveld 1, 6525ED Nijmegen, The Netherlands.*

Applying an IRIR double resonance technique in a seeded molecular jet, a rotationally cooled hot band spectrum of ethane has been recorded in the region of the C-H stretching fundamental ν_7 near 3000 cm^{-1} . A mixture of C_2H_6 and SF_6 in Ar is expanded through a slit nozzle. A 10 Watts cw CO_2 laser excites a single rotational level in the ν_3 manifold of SF_6 . Collisional relaxation redistributes the excited state population over many rovibrational levels of C_2H_6 . A continuously tunable F-center laser (FCL) then probes the changes in C_2H_6 population induced by the CO_2 laser.

No evidence has been found for hot bands starting from excited torsional states indicating that these levels are quickly deactivated by V-T transfer to the ground state in the collisional environment of the jet. Significant population of high rotational levels in the ground state demonstrate rapid conversion of internal rotation into end-over-end rotation of the molecule. The ν_9 state collects substantial population suggesting that this state is collisionally rather stable.

The observed hot bands are assigned to the two perpendicular components of the $\nu_7 + \nu_9(A_{1g} \oplus A_{2g} \oplus E_g) \leftarrow \nu_9(E_u)$ band. The spectrum appears to be heavily perturbed by dark state interactions in the upper level forcing us to analyse each K-stack separately. Rotational levels in the $\nu_7 + \nu_9$ state up to $J = 15$ and $K = 5$ have been least squares fitted to standard symmetric rotor expressions with an average standard deviation of 0.0014 cm^{-1} .

TG15

15 min 5:24

HIGH-RESOLUTION MICROWAVE AND INFRARED MOLECULAR-BEAM STUDIES OF THE CONFORMERS OF 1,1,2,2-TETRAFLUOROETHANE

S.C. Stone, L.A. Philips, *Department of Chemistry, Cornell University, Ithaca, NY 14853*; G.T. Fraser, F.J. Lovas, L.-H. Xu, *Optical Technology Division, National Institute of Standards and Technology, Gaithersburg, MD 20899*; S.W. Sharpe, *Molecular Sciences Research Center, Pacific Northwest Laboratory, Richland, WA 99352*.

High-resolution microwave and infrared molecular-beam spectra have been measured for 1,1,2,2-tetrafluoroethane (HFC134). For the higher-energy, polar, C_1 -symmetry, *gauche* conformer, microwave spectra have been recorded for the normal and mono- ^{13}C isotopomers and analyzed to determine a C-C bond length of 1.512(4) Å and a CCF angle of 109.7(3)°. A tunable microwave-sideband CO_2 laser and electric-resonance optothermal spectrometer have been used to measure the infrared spectrum of the ν_6 , C-C stretch of the *gauche* conformer near 906 cm^{-1} . Microwave-infrared double resonance and precise ground-state combination-differences provided by the microwave measurements guide the assignment of the spectrum. A *b*- and *c*-type spectrum is observed and fit to a Watson asymmetric-top Hamiltonian to within the experimental uncertainty of 0.3 MHz. The high quality of the fit and the similarity of the centrifugal distortion constants to the ground-state values indicate that the band is effectively unperturbed. A number of strong unassigned lines are present in the spectrum. These transitions do not display any microwave-infrared double resonance effect. The attribution of these transitions to the nonpolar *anti* conformer is ruled out since the transition intensities are sensitive to the field strength of the inhomogeneous electric field used to focus the molecules. Pulsed slit-jet diode-laser spectra have been recorded for the ν_{16} , *anti* conformer near 1127 cm^{-1} . An *a*- and *c*-type hybrid band is observed consistent with previous low-resolution assignments of this vibration to a B_u mode. A total of 522 non-blended transitions were assigned and fit to determine ground- and excited-state constants. The ground-state constants of $A = 5134.952(65)$, $B = 3148.277(27)$, and $C = 2067.106(43)$ MHz are the first experimental determination of rotational constants for this conformer.

TH01

15 min 1:30

ISOMERS OF SO₂: INFRARED ABSORPTION OF SOO IN SOLID AR

YUAN-PERN LEE, LI-SHUN CHEN, *Department of Chemistry, National Tsing Hua University, Hsinchu, TAIWAN 30043.*

Sulfur dioxide (SO₂) isolated in solid argon at 12K was irradiated with light at 193 nm from an ArF excimer laser. Preliminary results show that new absorption lines observed at 1006.1 and 739.9 cm⁻¹ are assigned to sulfur superoxide (SOO). Theoretical calculations using the B3-LYP/cc-pVTZ density functional method were carried out for SOO and cyclic SO₂; predicted vibrational wavenumbers are (1079, 763, and 472) and (1009, 739, and 682) cm⁻¹, respectively. Although observed wavenumbers fit better with those predicted for cyclic SO₂, the observed relative IR intensities and O-18 isotopic shifts are in excellent agreement with those predicted for SOO.

TH02

15 min 1:47

MATRIX ISOLATION SPECTROSCOPY OF Cl₃

W. G. LAWRENCE, R. FULGHUM, and M. C. HEAVEN, *Department of Chemistry, Emory University, Atlanta, GA 30322.*

A new visible emission system, tentatively assigned to the trichloride radical, has been observed in a solid Ar matrix. Cl₃ was prepared by photodissociation of HCl and permanent cage exit of the H atom in HCl/Cl₂ dimer trapping sites. Following photodissociation at 193 nm, a new emission at 470 nm was observed upon excitation at 308 nm. The intensity of the 470 nm emission increased with 193 nm irradiation time, and could be used to monitor the photodissociation dynamics of HCl in the argon matrix. Similarly the intensity of the Cl₂ A→X emission near 800 nm decreased with 193 nm irradiation. LIF and excitation spectra were used to characterize the trihalogen species. A model of the ionic states of Cl₃ is presented to describe the excitation spectra.

TH03

15 min 2:04

INFRARED SPECTROSCOPIC EVIDENCE FOR THE YLIDION (H₂CXH⁺) ISOMERS OF THE METHYL HALIDES TRAPPED IN SOLID NEON, CATHERINE L. LUGEZ, DANIEL FORNEY, MARILYN E. JACOX, AND KARL K. IRIKURA, National Institute of Standards and Technology, Gaithersburg, MD 20899.

When a Ne:CH₃X (X = F, Cl, Br) sample is codeposited at approximately 5 K with neon atoms that have been excited in a microwave discharge, the infrared spectrum of the resulting solid includes several absorptions which can be assigned to cation products. The identification of these products is aided both by studies of the isotopically substituted methyl halides and by *ab initio* calculations for both the conventional and the ylidion structures. In each of these systems, a prominent product absorption appears at a frequency intermediate between that of HX and of HX⁺. This and other absorptions which behave similarly on filtered tungsten and mercury-arc irradiation of the deposit have been assigned to the ylidion (H₂CXH⁺) isomer of the methyl halide cation. Earlier mass spectrometric studies^a had demonstrated H₂CFH⁺ to be more stable than CH₃F⁺ and had shown that the difference in stability of the two isomers is small for both the chloride and the bromide. An almost complete vibrational assignment has also been obtained for CH₃Br⁺.

^aJ. L. Holmes, F. P. Lossing, J. K. Terlouw, and P. C. Burgers, *Can. J. Chem.* **61**, 2305 (1983).

TH04

15 min 2:21

Spectroscopy of Carbon Cluster Anions in Argon Matrices

J. Szczepanski, S. Ekern and M. Vala

Carbon cluster anions (C_n^- with $n=3-18$) have been generated via a laser-induced graphite/Ar plasma with low energy electron beam access. The negative carbon cluster ions, partially extracted from a vaporization region, were trapped in an argon matrix at 20K. Absorption bands have been observed from 615.8nm to 6097.5nm. Shorter wavelength bands correspond well to the Ne matrix-isolated, mass-selected C_n^- through C_{20}^- cluster bands observed by Maier and coworkers^a. Longer wavelength bands fit the 0_0^0 electronic transitions expected by free electron molecular orbital (FEMO) model for the even carbon anion linear chain series well and extend it to C_{36}^- .

The asymmetric mode frequencies for small carbon cluster anions will be reported.

The significance of these measurements for observations from unknown species in interstellar space will be discussed.

^a P. Freivogel, J. Fulara, M.J. Jakobi, D. Forney, and J.P. Maier, J. Chem. Phys. 103, 54(1995)

Address of Szczepanski, Ekern and Vala: Department of Chemistry, University of Florida, Gainesville, FL 32611.

TH05

15 min 2:38

THEORETICAL STUDIES OF THE C_3H_2O POTENTIAL SURFACE: A MECHANISM FOR PROPYNAL FORMATION AND DEPLETION, S. P. EKERN, J. SZCZEPANSKI, AND M. VALA Department of Chemistry and The Center for Chemical Physics, University of Florida, Gainesville, FL 32611.

The C_3H_2O potential surface has been calculated at the HF/6-31G*, QCISD(T)/6-31G*, and MP2/6-31G* levels of the theory. Nineteen minima including the C_3-H_2O complex and fifteen transition states have been located. The predicted mechanism involves successive hydrogen shifts along the CCCO backbone with the necessary energy provided by photolysis. The presence and absence of experimentally observed C_3H_2O isomers under different photolytic conditions are satisfactorily explained.

TH06

15 min 2:55

LOW TEMPERATURE MATRIX ISOLATION STUDIES OF BORON TRIAZIDE

CHRISTOPHER J. LINNEN, JULANNA V. GILBERT, Department of Chemistry, University of Denver, Denver, CO 80208.

Boron triazide has been shown to form BN films upon photolysis at room temperature. (1) The photolysis mechanism is not understood, and low temperature matrix isolation experiments are planned that will probe the photolysis process. As a first step in this study, a boron triazide generator was attached to the inlet port of the cryostat in our laboratory. In the generator, stoichiometric flows of HN_3 and BCl_3 , both diluted in argon, are admitted to a 5 liter mixing bulb. The effluent from the mixing bulb is deposited on the cold KCl window in the cryostat. Infrared spectra of the matrices formed in this manner show the formation of B-N₃ containing species, and these will be presented and discussed. The results of ab initio calculations on $B(N_3)_xCl_y$ will be compared to these data.

1. R.L. Mulinax, G.S. Okin, R.D. Coombe; J. Phys. Chem. 99, 1995, 6295.

TH07

15 min 3:12

INFRARED SPECTRUM OF O_3^- ISOLATED IN SOLID NEON AND EVIDENCE FOR THE STABILIZATION OF $O_2 \cdots O_4^+$, CATHERINE L. LUGEZ, WARREN E. THOMPSON, AND MARILYN E. JACOX, Molecular Physics Division, National Institute of Standards and Technology, Gaithersburg, MD 20899.

When a Ne: O_3 sample is codeposited at approximately 5 K with neon atoms that have been excited in a microwave discharge, the most prominent infrared absorptions of the resulting solid are contributed by *trans*- and *cyc*- O_4^+ and by O_3^- . The failure to detect infrared absorptions of O_3^+ is consistent with the initial formation of that species in one or more dissociative excited states. The ν_3 absorption of O_3^- appears at 796.3 cm^{-1} , close to its position in earlier argon-matrix experiments in which photoionization of an alkali metal atom provided the electron source and in which diffusion of the atomic cation would result in the stabilization of appreciable $M^+O_3^-$. The identification of O_3^- isolated in solid neon is supported by observations of O_3^- generated from isotopically substituted Ne: O_2 : N_2O samples, also codeposited with excited neon atoms. An upper bound of 810 cm^{-1} is estimated for the gas-phase band center of ν_3 of O_3^- . Infrared absorptions which grow on mild warmup of the sample are tentatively assigned to an $O_2 \cdots O_4^+$ complex.

Intermission

TH08

15 min 3:45

Low Temperature Spectroscopy and Astrophysical Issues. The Interstellar Extinction

F. Salama, NASA-Ames Research Center, MS 245-6, Moffett Field, CA 94035.

The UV-to-NIR spectroscopic characteristics of neutral and ionized polycyclic aromatic hydrocarbons (PAHs) have been investigated using Matrix Isolation Spectroscopy (MIS). PAHs are considered very good candidates to account for the IR emission bands and the visible diffuse interstellar absorption bands (DIBs) seen in the interstellar medium. In the model dealing with the interstellar spectral features, PAHs, present as a mixture of radicals, ions and neutral species, are responsible for most of the IR spectral bands which are associated with UV-rich regions of space. Thus, it is crucial to assess their physical and chemical properties to understand how they influence the radiation and energy balance in space and the interstellar chemistry. A discussion of the physical and chemical conditions governing the production of ions in the interstellar medium and the implications for the role these species may play in the conversion of UV, visible and NIR interstellar radiation to infrared radiation is presented.

References: F. Salama in Low Temperature Molecular Spectroscopy, R. Fausto ed., NATO/ASI Series, Kluwer Acad. Pub., in press (1996); F. Salama, C. Joblin and L. Allamandola, J. Chem. Phys. 101, 10252 (1994); F. Salama and L. J. Allamandola, Nature 358, 42 (1992); *ibid*, J. Chem. Phys. 94, 6964 (1991).

TH09

15 min 4:02

Electronic Absorption Spectroscopy of Matrix Isolated Polycyclic Aromatic Hydrocarbon Ions. Contribution to Astrophysical Issues

F. Salama, NASA-Ames Research Center, MS 245-6, Moffett Field, CA 94035.

We have undertaken a series of experiments in which PAHs are isolated at 4.2 K in a Ne matrix and exposed to VUV irradiation. These experiments mimic the low temperature and density prevailing in the diffuse interstellar medium as well as the irradiation flux and offer a practical means to determine the spectroscopic properties of isolated PAH ions. A condition critical to the astrophysical application. This report will describe the results obtained with the smaller PAH candidates (up to coronene). The absorption spectra (180-900 nm range) of the molecular cations formed in a Ne matrix under VUV irradiation of the neutral precursor are reported together with the spectroscopic assignment of the associated vibronic band systems and their oscillator strengths. The potential contributions as well as limitations of MIS to long standing, unresolved problems in astrophysics are highlighted and illustrated with the results obtained on small PAH ions. Based on these preliminary results, we can now address the issue of gas phase measurements. We discuss the potential experimental approaches which could be used to probe the electronic/vibronic states of large aromatic ions.

References: F. Salama in Low Temperature Molecular Spectroscopy, R. Fausto ed., NATO/ASI Series, Kluwer Acad. Pub., in press (1996); F. Salama, C. Joblin and L. Allamandola, J. Chem. Phys. 101, 10252 (1994); F. Salama and L. J. Allamandola, Nature 358, 42 (1992); *ibid*, J. Chem. Phys. 94, 6964 (1991).

TH10

15 min 4:19

The Photolysis of Acetylene Halides Reaction with Oxygen

Mei-Lee Hwang, *Department of Chemical Engineering, Kaohsiung Polytechnic Institute, Taiwan, 84008*;
Yu-Ping Kuo, *Department of Applied Chemistry, Chia Nan Junior College of Pharmacy, Taiwan.*

The photolysis of chloro- and bromo-acetylene reactions at low temperature with Hg lamp are carried out. There is no new absorption band was observed after in-situ photolysis of acetylene halides in Ar matrix. With the presence of oxygen, several new bands were appeared. The new peaks at 2138 and 2342 cm^{-1} were assigned as CO and CO₂, respectively. Further work are essential for the assignment of the other new bands.

TH11

10 min 4:36

PHOTOCHEMISTRY OF MATRIX-ISOLATED TRIFLUORONITROSOMETHANE (CF₃NO) MEGAN MORGAN AND C.A. BAUMANN Department of Chemistry, University of Scranton, Scranton, PA 18510.

Mixtures of CF₃NO in rare gases were condensed at low temperatures and irradiated in the 633-670 nm region. Infrared spectra of the samples following irradiation indicate the presence of (CF₃)₂NONO, previously observed by Mason¹. Concentration and temperature dependence of the formation of this species are consistent with dissociation of the S₁ CF₃NO and migration of the nascent radicals to adjacent occupied matrix sites. While most of the bands assigned by Mason were observed to appear as the result of irradiation, no evidence of the Mason's 1803, 1830 cm^{-1} bands (assigned to the N=O stretch) was seen. The N=O stretch in this molecule may be as low as 1430 cm^{-1} , or may be hidden under the 1593.6 cm^{-1} band of the parent species.

¹ J. Mason, J. Chem. Soc. 1963, 4531.

TH12

15 min 4:48

EXPERIMENTAL MATRIX ISOLATION AND THEORETICAL AB INITIO STUDIES OF VIBRATIONAL SPECTRA OF HYDROGEN HALIDE COMPLEXES WITH STRONG NITROGEN BASES, KRYSZYNA SZCZEPANIAK, WILLIS B. PERSON, Department of Chemistry, University of Florida, Gainesville, FL 32611; and JANET E. DEL BENE, Department of Chemistry, Youngstown State University, Youngstown, OH 44555.

A systematic theoretical study of the structures and vibrational spectra of hydrogen-bonded complexes of hydrogen halides (HF, HCl, and HBr) with nitrogen bases at the MP2/6-31+G(d,p) level has been underway for some time^{a,b}. The basicity of these bases has been varied by changing the attached substituents to give complexes whose structures span the range of proton positions from Y-H...N neutral molecule complexes through proton shared Y...H...N bonds to proton transferred Y⁻...⁺H-N ion pairs. In this presentation we should like to begin reporting results from experimental studies of some of these complexes isolated in inert low temperature argon matrices. We shall show how the calculations help with the interpretation of these results, particularly with the complex pattern of very strong multiple absorption bands characteristically observed in the experimental spectra of many of these systems.

a) J. E. Del Bene, K. Szczepaniak, and W. B. Person, Chem. Phys. Lett., 247 (1995) 89.

b) J. E. Del Bene, K. Szczepaniak, and W. B. Person, Chemical Physics, in press, 1996.

TH13

15 min 5:05

INFRARED MATRIX ISOLATION STUDY OF THE REACTION OF TiCl₄ WITH LEWIS ACIDS; SPECTROSCOPIC CHARACTERIZATION OF Cl₃TiOCH₃

BRUCE S. AULT and JENNIFER B. EVERHART, Department of Chemistry, University of Cincinnati, P. O. Box 210172, Cincinnati, OH 45221-0172.

The reaction of TiCl₄ with NH₃, CH₃OH and other Lewis bases in twin jet and merged jet deposition systems followed by trapping in argon matrices at 14 K has been examined. With twin jet deposition, formation of the initial intermediate, a 1:1 complex, was observed in each case. In a merged jet reactor, the reaction of TiCl₄ with CH₃OH proceeded very rapidly to a second intermediate, monomeric Cl₃TiOCH₃, which has been observed for the first time. Identification and characterization was carried out by extensive isotopic labeling, and comparison to density functional calculations. Increasing the temperature of the merged jet region to above 200deg C led to the complete destruction of this species, and formation of additional products. Recent results on these and related systems will be reported.

TH14

15 min 5:22

MAGNETO-IR SPECTRA OF MATRIX-ISOLATED NiH AND NiH₂ MOLECULES AND THEORETICAL CALCULATIONS OF THE LOWEST ELECTRONIC STATES OF NiH₂, S. LI, R.J. VAN ZEE, W. WELTNER, JR., M.G. CORY AND M.C. ZERNER, Department of Chemistry and Quantum Theory Project, University of Florida, Gainesville, FL 32611.

Two $\Omega = 3/2 \leftarrow 5/2$ transitions (923,2560 cm⁻¹) were observed for NiH in solid argon and krypton at 4 K; both were shifted and broadened by magnetic fields of up to 4 T. Bands in the 1300-2000 cm⁻¹ were attributed to the stretching frequencies of NiH₂ (NiD₂, Ni HD) establishing it as a strongly bent molecule in its ground state. Calculations on NiH₂ indicate a stable bent (89.9° and R(NiH) = 1.482Å) singlet lower state nearly degenerate with respect to the triplet dissociation products but with a large intervening barrier. Calculated vibrational frequencies support the observed assignment.

TH15

10 min 5:39

Reactions of Laser Ablated Be Atoms with H₂O: Infrared Spectra of HOBeOH and H₂O-BeO in Solid Argon.

C. Thompson,^a and L. Andrews, *University of Virginia, Dept. of Chemistry, McCormick Road, Charlottesville, VA 22901.*

Products formed by reacting laser ablated Be atoms with H₂O included beryllium oxides seen in earlier Be + O₂ experiments^b as well as novel molecules mentioned above. Similar products arise from the formation of BeO in both systems. Once formed BeO may either react with H₂O to form HOBeOH or form the H₂O-BeO complex. Products were identified by several modes in excellent agreement with DFT calculations and provide interesting comparisons to beryllium oxides such as OBeO and Ar-BeO.^c HOBeOH is calculated to have an HOOH dihedral angle of 86° comparable to H₂O₂. The molecule also has a linear OBeO subunit whose antisymmetric stretch is observed about 81 cm⁻¹ to the blue of OBeO. Spectra for both species will be presented along with a brief comparison to the oxygen system.

^aCurrently a National Research Council-Naval Research Laboratory Associate.

Naval Research Laboratory. Code 6110 4555 Overlook Avenue SW Washington DC 20375-5342.

^bThompson, C. A.; Andrews, L. J. Chem. Phys. **100**, 8689 (1994).

^cThompson, C. A.; Andrews, L. J. Am. Chem. Soc. **116**, 423 (1994).

TH16

10 min 5:51

MATRIX INFRARED AND UV-VIS. STUDY OF REACTION BETWEEN Mg AND CH₃X; X = Br,Cl V.N.SOLOV'EV, A.V.NEMUKHIN, G.B.SERGEEV Chemistry department, Moscow State University, 119899, Moscow, Russia.

An attempt was made to detect directly mono- and bi- magnesium unsolvated Grignard reagents of type CH₃MgX and CH₃MgMgX. As the base for our experiments we used recent theoretical predictions of thermodynamical stability for such substances and calculations of vibrational spectra for Grignard reagents along with possible secondary products in the reaction of Mg with methylhalogens [1]. Calculations showed that differences in vibrational spectra of mono- and bi- magnesium Grignard reagents are strong enough to detect them experimentally.

Experiments were carried out by co-condensing resistively evaporated magnesium with both pure methylhalogens and their mixtures with argon at 11-12K. IR and UV-Vis spectra were recorded for various ratios of initial substances. Influence of annealing and UV-irradiation were also determined.

1. A.V.Nemukhin, V.N.Solov'ev, G.B.Sergeev, I.A.Topol Structure and spectra of methyl-magnesium Grignard complexes, Mendelev Communications 1996, N1 pp.5-7.

WA01**40 min 8:45****ROTATIONAL SPECTROSCOPY OF PRE-REACTIVE MULLIKEN COMPLEXES OF HALOGENS WITH LEWIS BASES.***A. C. LEGON, Department of Chemistry, University of Exeter, Stocker Road, Exeter, EX4 4QD, UK; , .*

Ground-state rotational spectra of a series of pre-reactive complexes $B \cdots XY$, where B is a Lewis Base and XY is a halogen or interhalogen molecule, have been observed. Complexes were formed, rapidly isolated and their spectra recorded before chemical reaction could occur between the components. To achieve this, a fast-mixing nozzle was used in combination with a Balle-Flygare F-T microwave spectrometer. Conclusions about the nature of the intermolecular interaction derived from analyses of the spectroscopic constants will be presented. In particular, an attempt will be made to answer the following question: Is it possible by careful choice of B and XY to identify examples of both types of Mulliken complex in the gas phase, namely those of the weak, outer type $B \cdots XY$ and those of the strong, inner type $[BX]^+ \cdots Y^-$ with significant charge transfer?

WA02**40 min 9:30****RECENT RESULTS ON HYDROGEN PEROXIDE AND NITRIC ACID***A. Perrin, Laboratoire de Physique Moléculaire et Applications, C.N.R.S., Université Pierre et Marie Curie, Case Courrier 76, Tour 13, 4, Place Jussieu, F-75252 Paris Cedex 05, France.*

Because of their atmospheric interest, hydrogen peroxide (H_2O_2) and nitric acid (HNO_3) have been the subject of numerous studies in the microwave, far-infrared, and infrared spectral ranges. Improved line positions and line intensities are indeed needed for reliable retrieval of atmospheric concentration profiles. Furthermore, these two molecules are of theoretical interest. The purpose of this paper is to compare the effect of a large amplitude motion for these two molecules which both exhibit a two-fold torsional motion but for which the description of the torsion is actually very different: for H_2O_2 , the motion is the torsion of the two "equal halves" O-H rotors around the O-O bond, while for HNO_3 , we are dealing with the torsional motion of the O-H bond relative to the much heavier NO_2 radical. In fact, even if the expression of the torsional potential is similar (we are dealing with only one two-fold motion) the symmetry considerations are very different, and the effects of the torsional motion, which increase with increasing energies, differ for these two molecules:

- For H_2O_2 the torsional motion induces both a splitting of the levels (tunneling through the trans-barrier) and a staggering (tunneling through the cis-barrier) of the already split levels.
- For HNO_3 , the torsional motion induces a splitting of the levels: in fact for the main $HN^{(16)}O_3$ isotopic species only a shift can be observed for some lines because of spin statistics reasons (the $^{(16)}O$ oxygen nucleus has a zero spin).

Finally, it is clear that both for H_2O_2 and HNO_3 these torsional effects become more complicated in the excited vibrational states due to the existence of numerous vibration-torsion resonances.

WA03**40 min 10:30****Structure and dynamics of large molecules and their van der Waals complexes by high resolution UV laser spectroscopy.**

W. LEO MEERTS, *Department of Molecular and Laser Physics, University of Nijmegen, P.O. Box 9010, 6500 GL Nijmegen, The Netherlands.*

The combination of a supersonic molecular beam expansion and a narrow band UV laser is a powerful tool in experimental molecular spectroscopy. It provides detailed information about the dynamics and structure of molecules and molecular complexes. Expanding volatilized organic molecules seeded in a carrier gas produces a cooling of the vibrational and rotational degrees of freedom. The low internal temperatures permit the stabilization of structural variants (tautomers or conformers) and the stabilization of molecular clusters (van der Waals and hydrogen bonded complexes).

Analysis of rotationally resolved laser induced fluorescence (LIF) spectra provides the molecular constants in both the ground and the electronically excited state, giving access to information about intramolecular and intermolecular bond lengths and their changes upon excitation.

In addition to the geometrical information, one can determine the orientation of the electronic transition moment vector in the molecular frame from the high resolution spectrum. This vector provides insight in the electronic charge migration or displacement that occurs during the transition. It is therefore related to the probability distribution functions in the involved electronic states.

Another interesting interaction is caused by the coupling of an internal hindered rotation with the overall rotation of the molecule. Full analysis of the spectra provide values for the barrier heights in the ground state and the excited state. The extent of complexity of the spectra depends strongly on the barrier heights, the direction of the internal rotation axis with respect to the overall inertial axis, and the (optical) selection rules (type of transition).

In the present talk first a short description is given of the experimental setup. A number of examples will be discussed to demonstrate the power of the method among others the triphenylamine and its van der Waals complex with argon, the 1-cyanonanththalene—triethylene complex, the tautomers of benzotriazole and the hydrogen bonded phenol—water complex.

WA04**40 min 11:15****HIGH-RESOLUTION SPECTROSCOPY OF SINGLE MOLECULES IN SOLIDS**

W. E. MOERNER, *Department of Chemistry and Biochemistry, University of California at San Diego, La Jolla, CA 92093-0340.*

A single impurity molecule in a solid is an exquisitely sensitive probe of the immediate local environment of the molecule (the "nanoenvironment"). Over the past few years, precision optical spectroscopy of the electronic transitions of individual, single impurity molecules in crystals and polymers has become an expanding field of study. Experimenters have observed a variety of fascinating physical effects, for example, the shifts in resonance frequency of a single molecule arising from nearby two-level-system transitions in the solid (spectral "diffusion"), the resonance Raman spectrum of a single molecule, quantum optical effects such as photon antibunching, and magnetic resonance of a single molecular spin (see *Science* 265, 46 (1994)).

The time-dependent resonance frequency of a single molecule (the spectral trajectory) provides information on dynamics of the nearby matrix which is not obscured by the usual need for ensemble averaging. Having such detailed dynamical trajectories of the spectral diffusion effect has stimulated theorists to produce a microscopic stochastic model for the local configurational degrees of freedom. In recent work, study of the spectral shifting behavior of single molecules has been extended to Shpol'skii matrices (frozen alkanes) in which a two-state or few-state behavior has been observed. This behavior can be followed with a fluorescence microscope in real time at video frame rates. Motivated by the need for higher signal-to-noise ratios and increased spatial resolution, we have used a low-temperature near-field optical source of subwavelength dimensions to record excitation spectra of single molecules located below the surface of a solid sample ^a.

^aW. E. Moerner, T. Plakhotnik, T. Irngartinger, U. P. Wild, D. W. Pohl, and B. Hecht, *Phys. Rev. Lett.* 73, 2764 (1994)

WE01

10 min 1:30

HIGH RESOLUTION ANALYSIS OF THE ν_2 , $2\nu_2$, $3\nu_2$, ν_1 AND ν_3 BAND OF HYDROGEN TELLURIDE, O. POLANZ, H. BÜRGER, BUGH Wuppertal, FB 9 Anorganische Chemie, Gaußstr. 20, D-42097 Wuppertal, Germany, J.-M. FLAUD, Ph. ARCAS, M. BETRENCOURT, LPMA, CNRS, Université P. et M. Curie, 4, Place Jussieu, F - 75252 Paris Cedex 05, France, W.J. LAFFERTY, Optical Technology Division, NIST, Gaithersburg, MD 20899, USA.

The vibration-rotation absorption bands ν_2 , $2\nu_2$, $3\nu_2$, ν_1 and ν_3 of H_2Te have been analyzed using high resolution Fourier transform spectra of natural and ^{130}Te monoisotopic material. The rotational levels of the upper states $(\nu_1\nu_2\nu_3) = (010)$, (020) and (030) have been very satisfactorily fit using a Watson-type Hamiltonian. It proved however necessary to include Coriolis interaction terms in the Hamiltonian matrix to calculate to within the experimental accuracy (0.0002 cm^{-1}) the rotational levels of the two interacting states (100) and (001) .

From these fits, accurate upper states Hamiltonian constants have been derived for the seven most abundant tellurium isotopes. These constants have then been used to derive a preliminary equilibrium structure for H_2Te .

WE02

15 min 1:42

ANALYSIS OF THE FIRST AND SECOND TRIADS OF H_2S FROM 2200 TO 4100 CM^{-1}

L. R. Brown, J. A. Crisp, D. Crisp, *Jet Propulsion Laboratory, California Institute of Technology, 4800 Oak Grove Drive, Pasadena, California 91109*; A. Perrin, *Laboratoire de Physique Moléculaire Applications CNRS, Université Pierre et Marie Curie Bte 76, 4 Place Jussieu 75252 Paris Cedex 05, France*; A. D. Bykov, O. V. Naumenko, M. A. Smirnov and L. N. Sinita, *Institute of Atmospheric Optics, SB, Russian Academy of Science, 634055, Tomsk, Russia*.

The 1800 - 5400 cm^{-1} region of H_2S was recorded at 0.011 cm^{-1} resolution using the McMath Fourier transform spectrometer located at Kitt Peak National Observatory. The positions of the first triad [$2\nu_2$, ν_1 and ν_3] near 4 μm and the second triad [$3\nu_2$, $\nu_1 + \nu_2$ and $\nu_2 + \nu_3$] near 2.7 μm were obtained for H_2^{32}S , H_2^{34}S and H_2^{33}S . The experimental upper states were fitted to the A-reduced Watson Hamiltonian to determine precise sets of rotational constants and Fermi and Coriolis coupling parameters. Line intensities of H_2^{32}S up to $J = 17$ and $K_a = 12$ were measured and modelled to $\pm 2.5\%$ using the 564 intensities of the first triad and 526 intensities of the second triad. The coefficients of the transformed moment expansion were obtained, corresponding to band strengths in $\text{cm}^{-2}/\text{atm}$ at 296 K of: 0.33 for $2\nu_2$, 0.45 for ν_1 and 0.12 for ν_3 , 0.03 for $3\nu_2$, 1.82 for $\nu_1 + \nu_3$ and 2.87 for $\nu_2 + \nu_3$.

Part of the research reported in this paper was performed at the Jet Propulsion Laboratory, California Institute of Technology, under contract with the National Aeronautics and Space Administration.

WE03

10 min 1:59

FOURIER TRANSFORM INFRARED SPECTRA OF FORMALDOXIME: THE ν_7 , ν_9 , ν_{11} , ν_{12} , and $2\nu_{12}$, BANDS

G. DUXBURY AND G. RITCHIE, *Department of Physics and Applied Physics, Strathclyde University, Glasgow G4 0NG, Scotland, UK*; R. A. BANNAI, *Department of Physics, University of Bahrain, P.O. Box: 32038, Bahrain.*; S. KLEE, *Physikalisch-Chemisches Institute der Justus-Liebig Universität, D-6300 Giessen, Germany.*

A first full rotational analysis of high resolution gas phase spectra of the lowest frequency fundamental bands, ν_9 and ν_{12} , of formaldoxime, CH_2NOH , has been completed. In addition the weak ν_7 fundamental has been analysed at medium resolution, and the complex structure of the bands in the ν_{11} and $2\nu_{12}$ region has been revealed. It is shown that the complexity of the spectrum of the latter region is due to Coriolis interaction between the overtone $2\nu_{12}$ and the fundamental band ν_{11} . The region covered in this analysis is from 8-30 μm . Since the molecule has C_s symmetry, in principle all the bands of A' symmetry are AB hybrids. Although the ν_4 , ν_5 , ν_6 , and ν_8 fundamental bands described previously are predominantly A type, the ν_7 band is found to be almost a pure B-type band. The ν_{11} and ν_{12} bands are C-type bands. The band origins (cm^{-1}) are ν_7 1157.282 ν_9 530.01785 ν_{11} 772.78, ν_{12} 397.68499 and $2\nu_{12}$ 778.517.

WE04

15 min 2:11

LOW TEMPERATURE FTIR SPECTRA OF METHYL SILANE

CHANGHONG XIA AND GEOFFREY DUXBURY, *Department of Physics and Applied Physics, Strathclyde University, Glasgow G4 0NG, Scotland, UK*; DAVID NEWNHAN AND JOHN BALLARD, *Atmospheric science division, Space science Department, Rutherford Appleton Laborator, Chilton, Didcot, OX11 0QX, UK.*

The fundamental vibrational bands of methyl silane (CH_3SiH_3) ν_1 , ν_2 , ν_7 , and ν_8 have been recorded at 203K and 77K using both conventional absorption cells and also the RAL collisional cooling cell, at resolutions of up to 0.0017 cm^{-1} . In the low temperature spectra, the torsional splitting of the rotational transitions, which is obscured in the room temperature spectra, has been resolved and assigned in the majority of cases. Previously missassignment of the ν_1 Q branch splitting has corrected. Rotation constants of methyl silane and the torsional barrier for the different excited states have been determined

WE05

15 min 2:28

VIBRATIONALLY EXCITED HCl AND HF PRODUCED FROM PHOTODISSOCIATION OF CH_3CFCl_2 AT 193 NM BY MEANS OF TIME-RESOLVED FTIR

PEY-SHIUN YEH, YUAN-PERN LEE, *Department of Chemistry, National Tsing Hua University, Hsinchu, TAIWAN 30043.*

We have determined the emission spectra of HF and HCl at various interval safter photolysis of CH_3CFCl_2 at 193 nm by means of time-resolved Fourier-transform spectroscopy. Typical resolution used was 1.0 cm^{-1} with acquisition intervals of 5 μs for 100 data points, and the signal was averaged for 60-80 laser pulses at each scan step. IR emission was collected by a Welsch-type cell and focused to the entrance aperture of the emission port of the spectrometer. Emission of HF from $1 \leq v \leq 5$ was observed, with intensity peaked at varied time intervals after photolysis. Fitting the temporal profiles of emission from each vibrational level yielded rates of quenching and nascent population. Preliminary results indicate that the nascent vibrational population distribution of HF is 0.42:0.31:0.14:0.08:0.05 for $v = 1-5$, respectively. Measurements of rates of quenching at varied partial pressure of CH_3CFCl_2 yielded rate coefficients of quenching of HF ($1 \leq v \leq 4$) by parent molecule. The results are compared with those reported for photolysis of similar molecules. Emission of HCl ($v \leq 4$) was also observed after photolysis of CH_3CFCl_2 . The formation mechanism and associated kinetics will be presented.

WE06

15 min 2:45

FTIR DETECTION OF P_4O_{10} FROM COMBUSTION OF ELEMENTAL PHOSPHORUS

R.C. MOWREY, C.H. DOUGLASS^a, B.A. WILLIAMS, and H.D. LADOUCEUR, *Chemistry Division, Code 6100, Naval Research Laboratory, Washington, DC 20375-5000.*

The emission spectra of gaseous combustion products of elemental phosphorus in air and in inert atmospheres with added oxygen were measured using Fourier transform infrared spectroscopy. Features corresponding to three fundamental and one overtone vibrational modes of P_4O_{10} were assigned. To our knowledge, this is the first assignment to P_4O_{10} of infrared emissions in a reacting system. In conjunction with the experimental measurements, the structures, vibrational frequencies, and vibrational intensities of P_4O_{10} and P_4O_6 were computed using *ab initio* electronic structure methods. The calculations were performed at the Hartree-Fock level using a double zeta plus polarization basis set. The predicted vibrational spectra are in good agreement with the observed spectra and with previous absorption measurements of P_4O_{10} and P_4O_6 .

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WE07

15 min 3:02

Interaction of vibrational fundamental and combination states of ethylene in 3 μm region

Boris G. Sartakov, *General Physics Institute RAS, Vavilov str. 38, 117942, Moscow, Russia*; Jos Oomens and Jörg Reuss, *Department of Molecular and Laser Physics, Catholic University of Nijmegen Toernooiveld 1, 6525ED Nijmegen, The Netherlands.*

Formalism of symmetry groups has been developed and applied to expand the vibrational-rotational Hamiltonian and operator of dipole moment of ethylene into a power series of annihilation and creation operators as well as angular momentum operators. This approach allows to characterize every term of the series by its specific order in which the operators appear.

The first analysis of the 3 μm spectra reveals the strong coupling between ν_9 , ν_{11} , $\nu_2 + \nu_{12}$ and $2 \cdot \nu_{10} + \nu_{12}$ yielding shifts of about 0.01 cm^{-1} for some low J and K lines of C_2H_4 . We find that significant shifts are due to perturbations of ν_9 rotational-vibrational levels via 3rd order b-type Coriolis interaction with the $\nu_3 + \nu_8 + \nu_{12}$ rotational levels.

A prominent borrowing of transition dipole moment is predicted for some otherwise dark rovibrational lines of the $\nu_3 + \nu_8 + \nu_{12}$ band. These satellite lines have been found and assigned in low temperature spectra of ethylene recorded by the F-center laser spectrometer in a jet and afterwards in room temperature spectra recorded earlier by the difference-frequency laser spectrometer [1] and recently by the FTIR spectrometer in the Giessen group. The fitting of interaction parameters with the mentioned perturbations leads to a standard deviation of $2 \cdot 10^{-3} \text{ cm}^{-1}$, for low J lines of ethylene. The leading coupling parameters in the pentade ν_9 , ν_{11} , $\nu_2 + \nu_{12}$, $2 \cdot \nu_{10} + \nu_{12}$ and $\nu_3 + \nu_8 + \nu_{12}$ are shown in the table

States	Type	Value (cm^{-1})
ν_{11} and $\nu_2 + \nu_{12}$	cubic anharmonicity	45.459(2)
$\nu_2 + \nu_{12}$ and $2 \cdot \nu_{10} + \nu_{12}$	cubic anharmonicity	-10.721(2)
ν_9 and ν_{11}	1 st order Coriolis interaction	-0.130(3)
ν_9 and $\nu_3 + \nu_8 + \nu_{12}$	3 rd order Coriolis interaction	-0.022(8)

The last parameter approximately describes, too, the perturbations between $\nu_9 + \nu_{10}$ and $\nu_3 + \nu_8 + 2 \cdot \nu_{10}$, observed in the hot bands spectra.

[1] A.S.Pine *Tunable Laser Survey of Molecular Air Pollutants, Final Report NSF/ASRA/DAR 78-24562*, MIT, Lexington, Mass. (1980)

WE08

15 min 3:40

THE CARBODIIMIDE SPECTRUM IN THE WAVENUMBER RANGE OF 450-1000 cm⁻¹ AND IN THE THz REGION

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Carbodiimide, HNCNH, is an accidentally nearly symmetric top molecule ($\kappa = -0.99999537$) and it undergoes internal rotation hindered by a *cis* and a *trans* energy barrier of nearly equal height of about 2070 cm⁻¹. This internal motion leads to torsional splittings of the rotational energy levels, which show an unusual dependence on the K_a rotational quantum number. The strong coupling between the torsional and the HNC bending motion leads to rotationally dependent contributions to the effective torsional potential function. To extend our knowledge about these complex internal motions and the structure of the molecule we recorded the spectrum of the equilibrium mixture of carbodiimide and cyanamide, H₂NCN, with a Bruker IFS 120HR in the range from 450 to 1000 cm⁻¹. Unfortunately the strong dominance of cyanamide (approximately 115:1 at 110°C) makes it very difficult to identify the torsional fundamental vibration. However, the antisymmetric HNC-bending fundamental could be analysed. To support the assignment procedure *ab-initio* calculations using the CCSD(T) method had been carried out.

Spectra of the terahertz region offer the opportunity to study another remarkable property of the molecule, namely the recently observed inversion of the $K_a = 2$ energy levels^a and the shift of the $K_a = 1$ levels due to a centrifugal distortion interaction with $\Delta K_a = 4$. We have now measured and analysed the 7Q_1 branch at 1.1 THz. The analysis of the terahertz data and the infrared data in the light of the recent *ab-initio* calculations will be presented.

^aV. Wagener, M. Winnewisser, M. Bellini, J. Mol. Spectrosc. **170**, 323 (1995)

WE09

15 min 3:57

INFRARED EMISSION SPECTROSCOPY OF THE COINAGE METAL HYDRIDES AND DEUTERIDES, F. CHARRON, S.-K. LEE^a, AND P.F. BERNATH Department of Chemistry, University of Waterloo, Waterloo, ON N2L 3G1

Cu, Ag and Au were each vaporized in a carbon tube furnace in the presence of about 100 torr of the H₂ or D₂. Vibration rotation emission spectra of CuH, CuD, AgH, AgD, AuH and AuD were recorded with a high resolution Bruker Fourier transform spectrometer. Improved molecular constants were determined for each of the six molecules.

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WE10

15 min 4:14

HIGH RESOLUTION INFRARED SPECTROSCOPY OF THE ν_5 AND ν_7 BANDS OF HEXAFLUOROETHANE

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The ν_5 and ν_7 fundamental bands of hexafluoroethane were observed using two molecular beam techniques: pulsed slit-jet, diode laser spectroscopy, and continuous slit-jet, Fourier transform spectroscopy. The estimated rotational temperature of both beams is on the order of 10 K. Preliminary analysis of the ν_5 parallel band shows a regular progression of strong $K = 0$ transitions in the P , Q , and R -branches; other sub-bands are heavily perturbed. The band origin is at $1117.1098(5) \text{ cm}^{-1}$, $B'' = 0.06140(9) \text{ cm}^{-1}$, and $B' = 0.061641 \text{ cm}^{-1}$ for the prolate symmetric top molecule. The ν_7 perpendicular band is centered at 1253 cm^{-1} and shows a congested series of RQ and PQ sub-branches. Spectra from both spectrometers and a detailed ro-vibrational analysis will be presented for both bands.

WE11

15 min 4:31

TORSION-VIBRATION INTERACTIONS IN THE CH_3 -ROCKING AND OH-BENDING FUNDAMENTALS OF C-13 METHANOL

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A review is presented of our recent work on the study of the molecular interactions observed in the CH_3 -rocking and OH-bending bands of C-13 methanol. The main aim was to find the interaction constants and to estimate the contributions due to the torsional motion. The modelling was done using a Marquardt algorithm and a second order perturbation theory approach.

The frequent Fermi mixing between states of the OH-bending and the first torsionally excited CH_3 -rocking modes make it essential to study these bands jointly and not individually ^a. The pattern of torsion-rotation energies for the OH-bending mode is inverted relative to that of the ground state, implying that the usual Hamiltonian used successfully for the ground state cannot describe the excited state energy manifold.

With our new findings, we hope to contribute to better understanding of the torsion-vibration energy structure of the bending modes of methanol.

^aA. Predoi, R.M. Lees, G. Mellau, and J.W.C. Johns, 50th Symp. on Mol. Spectrosc., 1995, Paper RA12.

WE12

15 min 4:48

A COMPLETE STRUCTURE OF THE *ANTI* ROTAMER OF 1,2-DIFLUOROETHANE FROM HIGH RESOLUTION INFRARED SPECTROSCOPY, NORMAN C. CRAIG, ANTHONY CHEN, AND KI HWAN SUH, Department of Chemistry, Oberlin College, Oberlin, OH 44074; GEORG C. MELLAU, STEFAN KLEE, Physikalisch-Chemisches Institut der Justus-Liebig-Universität, Heinrich Buff Ring 58, D-35392 Giessen, Germany

In the high resolution infrared spectra of both the $^{13}\text{C}_2$ and the d_4 isotopomers of 1,2-difluoroethane, a B-type band has been analyzed. This band, which is due largely to antisymmetric CF bending, is at 279.410 cm^{-1} for the $^{13}\text{C}_2$ species and at 264.257 cm^{-1} for the d_4 species. From fitting 663 ground state combination differences (GSCD) to a Watson-type Hamiltonian, GS rotational constants for the $^{13}\text{C}_2$ species are $A = 1.022398(2)$, $B = 0.128825(8)$, and $C = 0.119682(8) \text{ cm}^{-1}$ with $\kappa = -0.9798$. From fitting 950 GSCDs, the GS rotational constants for the d_4 species are $A = 0.6902091(11)$, $B = 0.1253009(6)$, and $C = 0.1154862(6) \text{ cm}^{-1}$ with $\kappa = -0.9658$. Upper state constants have also been fitted to the central parts of the bands. From the GS constants for the d_0 species^a as well as for the $^{13}\text{C}_2$ and d_4 species, a largely r_s structure has been found. These structural parameters will be compared with those of the *gauche* rotamer found from microwave spectroscopy.^b

^aN. C. Craig, S. Klee, G. C. Mellau, B. P. Winnewisser and M. Winnewisser, to be published.

^bH. Takeo, C. Matsumura and Y. Morino, *J. Chem. Phys.* **97**, 4205 (1986).

WE13

10 min 5:05

ANALYSIS OF A C-TYPE BAND OF *TRANS*-1,2-DICHLOROETHYLENE- $^{35}\text{Cl}_2$ IN NATURAL ABUNDANCE IN THE HIGH RESOLUTION INFRARED SPECTRUM, NORMAN C. CRAIG AND EMILIO L. MORALES, Department of Chemistry, Oberlin College, Oberlin, OH 44074; GEORG C. MELLAU AND STEFAN KLEE, Physikalisch-Chemisches Institut der Justus-Liebig-Universität, Heinrich Buff Ring 58, D-35392 Giessen, Germany

We have found that subbands in the C-type band at 897.950 cm^{-1} in the high resolution infrared spectrum of *trans*-1,2-dichloroethylene can be analyzed separately for the $^{35}\text{Cl}_2$ and $^{35}\text{Cl}^{37}\text{Cl}$ isotopomers in natural abundance with the aid of the Giessen Loomis-Wood program. Consequently, it is unnecessary to synthesize isotopically pure chlorine species in order to determine the structure of this *nonpolar* molecule by high resolution infrared spectroscopy. For the $^{35}\text{Cl}_2$ isotopic species 874 ground state combination differences (GSCD) have been fitted to a Watson-type Hamiltonian. The GS rotational constants are $A = 1.7472665$ (55), $B = 0.5157118$ (5), and $C = 0.5008142$ (5) cm^{-1} with $\kappa = -0.9982$. Based on the GS constants a preliminary comparison with the structure of the *cis* isomer^a will be made. Work on the analysis of the corresponding bands of the $^{35}\text{Cl}^{37}\text{Cl}$ species and the $^{35}\text{Cl}_2\text{-d}_2$ species is in process.

^aH. Takeo, M. Sugie and C. Matsumura, *J. Mol. Struct.* **190**, 205 (1988).

WE14

10 min 5:17

THE IR SPECTROSCOPY INVESTIGATION OF THE HYDRIDE-WATER INTERMOLECULAR INTERACTION IN LIQUID AND GASEOUS PHASES, P. SENNIKOV, V. SHKRUNIN, D. RALDUGIN, AND V. CHORSHEV, Institute of Chemistry of High-Purity Substances, Russian Academy of Sciences, Nizhny Novgorod, 603600 Russia

The dilute solutions of water in liquefied hydrides of Group V and VI elements (PH_3 , AsH_3 , H_2S , and H_2Se) have been studied by means of conventional IR spectroscopy method at 293K. The analysis of water fundamentals as going from gas phase (free state of water molecules) to the solutions (weak H-bonded complexes of water with hydride's molecules) has been given. The relative strength of H-bonds in 1:2 complexes water-hydride was estimated. It was found that the hydrides of Group VI elements on the one hand and of the 2nd row on the other are slightly better proton acceptors as compared with the hydrides of the Group V and 3d row elements.

The half-width at half-maximum (HWHM) of the line at $1675, 1172\text{ cm}^{-1}$ of water impurity in gaseous hydrides GeH_4 , H_2Se , and NH_3 , as well as in oxygen and argon has been measured by tunable laser IR spectrometer at 293K. Taking into account the invariability of the Doppler contribution and of the gas pressure in the cell, the difference by the more as order of magnitude of the HWHM and of the broadening factor values for different gases can point to the change in the character of the intermolecular interaction as going from the water in nonpolar gases (van-der-Waals interaction) to water in polar hydrides of selenium and nitrogen (H-bonding).

WE15

15 min 5:29

RAMAN STUDY OF MOLECULAR VIBRATIONAL RELAXATION IN H-BONDED SYSTEMS

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The idea of the paper is a comparative study of intermolecular H-bond interaction influence on a shape and a shift of bands which correspond to vibrations of two types: 1) vibrations which are subjected to H-bond influence directly; 2) vibrations which are affected by H-bond indirectly. A study of feature of H-bond influence on a shape of Fermi-duplicates was performed too. Solvents with weak, intermediate and strong H-bond were selected. Principal results: 1) There isn't direct correlation between energy of specific interaction and shifts of CH-bands. 2) Intramolecular vibrational redistribution is weakly subjected to influence of weak and intermediate specific interactions. In the case of a strong H-bond intermolecular vibrational exchange predominates over intramolecular process.

SPECTROSCOPIC EVALUATION OF THE STRUCTURE AND DYNAMICS OF THE HYDROGEN BONDS IN DIFFERENT CRYSTAL MODIFICATIONS OF POTASSIUM BIIODATE

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The $\text{KIO}_3 \cdot \text{HIO}_3$ crystals belong to the family of acidic iodate compounds which is well-known for its ferroelectric phase transitions and has four crystal modifications. Here we report the results of IR and Raman study of vibrational spectra ($4000\text{--}60\text{ cm}^{-1}$) of α and δ -modifications in the temperature range from 300 to 13 K. The α - $\text{KIO}_3 \cdot \text{HIO}_3$ crystal ($P2_1/b$ space group, $z=4$ at room temperature) is built of two nonequivalent sets of dimers $\text{IO}_3 \cdots \text{H} \cdots \text{O}_3\text{I}$, joined by strong symmetric hydrogen bond ($\text{O} \cdots \text{O}$ distance is about 2.5 \AA). At 223 K (T_c) the ferroelectric phase transition occurs in this crystal. The stable δ -modification (space group $Fdd2$, $z=24$ at room temperature) is formed from structure units of three distinct types: I_2O_5 and $\text{I}_2\text{O}_5(\text{OH})$, which are joined by the H-bond network. In order to understand the normal modes of vibrations in α - $\text{KIO}_3 \cdot \text{HIO}_3$ and δ - $\text{KIO}_3 \cdot \text{HIO}_3$, we have carried out lattice dynamics calculations using a generalized valence force field for the dimers $[\text{H}(\text{IO}_3)_2]^-$ and other structure units. The introduction of the translation and libration coordinates related to the normal coordinate analysis leads to a precise assignment of the frequencies and shows that both stretching and bending vibrations of IO_3 groups are strongly coupled with the translational vibrations of the hydrogen atom in case of α -modification. In the case of δ -modification those vibrations are localized on separate I—O bonds. A comparative analysis of the vibrational spectra and structure is presented. On the base of analysis of vibrational spectra and according to measurements^a of pressure dependencies of the ^{127}I NQR spectra at 77 K it was concluded that the mechanism of ferroelectric phase transition in α -modification of potassium biiodate crystal involves the proton ordering in the double-well potential at T_c .

^aA.I.Barabash, J. Mol. Struct., **270**, 517 (1992).

WF01**15 min 1:30****STRUCTURE OF LiOH FROM MICROWAVE SPECTROSCOPY AND *AB INITIO* THEORY**

A.J. APPONI, L.M. ZIURYS, *Department of Chemistry, Arizona State University, Tempe, AZ 85287*; F.-M. TAO, *Department of Chemistry, California State University, Fullerton, CA 92634*; K. HIGGINS, W. KLEMPERER, *Department of Chemistry, Harvard University, Cambridge, MA 02138*.

Measurements of rotational transitions between 100 and 500 GHz are reported for LiOH and LiOD. The observed transitions are compared to transitions calculated by the collocation method using a potential energy surface from an *ab initio* electron structure calculation at the MP4 level. The agreement between theory and experiment is satisfactory and establishes the minimum energy structure to be linear. The calculated potential for bending is found to be relatively flat but no evidence for any nonlinear minimum is found. The equilibrium Li-O internuclear distance calculated is 1.5% greater than observed. This deviation is virtually identical to that found for LiF using the same level of theory.

WF02**15 min 1:47**

THE MILLIMETER/SUB-MM WAVE SPECTRUM OF THE FeCl RADICAL ($X^6\Delta_1$),
 B.-Z. LI, M. D. ALLEN, AND L. M. ZIURYS, *Department of Chemistry & Biochemistry, Arizona State University, Tempe, Arizona 85287-1604*.

The pure rotational spectrum of the FeCl radical in its $X^6\Delta_1$ state has been recorded using millimeter/sub-mm direct absorption spectroscopy. FeCl radical was created by the reaction of Cl_2 and iron vapor, produced in a Broida-type oven. Twenty rotational transitions were recorded in the frequency range 200-500 GHz. All six spin-orbit components were observed, and lambda-doubling in the $\Omega = 3/2, 1/2$, and $-1/2$ ladders was resolved. Spectroscopic constants have been determined, including rotational, certain spin-orbit, spin-spin, and lambda doubling parameters.

WF03**15 min 2:04**

^{19}F Spin-rotation Constants and Chemical Shifts of Unstable Molecules from their Microwave Spectra

Bethany Gatehouse, Holger S. P. Müller^a, and Michael C. L. Gerry, *University of British Columbia, Department of Chemistry, 2036 Main Mall, Vancouver, B.C., Canada, V6T 1Z1*.

The inherently high resolution of the pulsed molecular beam-microwave Fourier transform (MWFT) technique allows spin-rotation coupling constants to be routinely determined from small hyperfine splittings in rotational transitions. The relationship between the spin-rotation coupling constants and the chemical shielding of a given nucleus has been well established^b; these constants can be used to calculate the individual components of the chemical shielding tensor as well as the average chemical shift. Thus, shielding data for unstable and semi-stable molecules, which are relatively easily studied by MWFT, can be obtained.

Several ^{19}F containing species have been prepared using an electric discharge. Their microwave spectra have been measured in the 4-26 GHz frequency range and the determined diagonal components of the nuclear spin-rotation tensors have been used to calculate the chemical shielding tensors. One such molecule that is of particular interest is sulphur difluoride. Two of its spin-rotation coupling constants were found to be negative. Negative fluorine spin-rotation coupling constants are very unusual, and have been seen before only for the interhalogens^c ClF , BrF , and IF . These findings are consistent with previous *ab initio* calculations^d and an NMR experiment^e.

^apresent address: Jet Propulsion Laboratory, California Institute of Technology, Pasadena, California, 91109

^bW. H. Flygare, *J. Chem. Phys.*, **41**, 793, (1964)

^cH. S. P. Müller and M. C. L. Gerry, *J. Chem. Phys.*, **103**, 577, (1995); and references therein

^dM. Schindler, *J. Chem. Phys.*, **88**, 7638, (1988)

^eW. Gombler, J. Schaebs, and H. Willner, *Inorg. Chem.*, **29**, 2697, (1990)

WF04

15 min 2:21

The Pure Rotational Spectrum of Magnesium Sulfide Produced by Laser Ablation

Kaley A. Walker and Michael C. L. Gerry, *Department of Chemistry, University of British Columbia, Vancouver, B.C., Canada, V6T 1Z1.*

A new laser ablation system has been built that incorporates a Smalley-type ablation nozzle^a into our existing pulsed molecular beam-microwave Fourier transform (MWFT) spectrometer. The second harmonic of a Nd:YAG laser is used to ablate a metal rod, which is located in the throat of a nozzle. The rod is rotated to provide a fresh surface for each laser pulse. This ablation setup has been mounted into one of the cavity mirrors, so that the molecular beam travels parallel to the direction of microwave propagation. This configuration results in linewidths of ~ 10 kHz FWHM.

To test this new system, the microwave spectrum of MgS has been measured. The $J = 1 - 0$ transitions of 4 isotopomers, including the $^{25}\text{Mg}^{32}\text{S}$ isotopomer which exhibits nuclear hyperfine structure due to the ^{25}Mg nucleus, have been observed at 16 GHz. Improved rotational and centrifugal distortion constants have been obtained for the main isotopomer, $^{24}\text{Mg}^{32}\text{S}$, by fitting the $J = 1 - 0$ transition with data from a previous millimeter wave study^b. From the isotopic data, the internuclear distance was calculated. The ^{25}Mg nuclear quadrupole coupling constant has also been determined. We believe this to be the first measurement of the microwave spectrum of a metal sulfide produced by laser ablation.

^aT. G. Dietz, M. A. Duncan, D. E. Powers and R. E. Smalley, *J. Chem. Phys.* **74**, 6511 (1981)

^bS. Takano, S. Yamamoto and S. Saito, *Chem. Phys. Lett.* **159**, 563 (1989)

WF05

15 min 2:38

ROTATIONAL SPECTRA OF JET-COOLED ION COMPLEXES

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Microwave spectra of complexes bearing molecular ions, $\text{Ar-D}_3^+/\text{HD}_2^+$ and Ar-HCO^+ , were explored in a jet-cooled condition. The ionic complexes were formed by a pulsed electric discharge in a supersonic expansion. Their transitions were observed in the centimeter-wave region (7-40 GHz) with a Fourier-transform microwave spectrometer, guided by the previous millimeter-wave study in a static cell^a or the recent infrared photodissociation study in a mass-selected ion beam.^b

For Ar-HCO^+ , rotational transitions of mono-substituted species on H, C, and O were also measured. The isotopic substitution has confirmed the linear $\text{Ar} \cdots \text{H-C-O}$ configuration with the $\text{Ar} \cdots \text{H}$ distance of 2.13 Å. The centrifugal-distortion constant for Ar-HCO^+ is two order of magnitude smaller than that for Ar-HCN , indicating much stronger binding in the ionic complex than the isoelectronic neutral counterpart.

^aM. Bogey, H. Bolvin, C. Demuynck, and J. L. Destombes, *Phys. Rev. Lett.* **58**, 988 (1987).

^bS. A. Nizkorodov, O. Dopfer, T. Ruchti, M. Meuwly, J. P. Maier, and E. J. Bieske, *J. Phys. Chem.* **99**, 17118 (1995).

WF06

15 min 2:55

NEW MEASUREMENTS OF THE PROTON MIGRATION TUNNELING SPLITTING IN THE ROTATIONAL SPECTRUM OF $C_2H_3^+$

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New measurements have been carried out in the rotational spectrum of $C_2H_3^+$ using a negative glow discharge. An improved resolution made it possible to determine the value of the tunneling splitting for one more line than in previous studies^{a,b}. Microwave data have been analyzed with a formalism based on the Internal-Axis-Method-like approach set-up to treat the water dimer^c. The three experimentally resolved splittings were predicted within the experimental resolution around the measured values. Calculations also provided us with more information about the tunneling path along which the three protons migrate^d.

^aM. Bogey, M. Cordonnier, C. Demuyne and J. L. Destombes, *Astrophys. J.* **399**, L103 (1992).

^bM. Bogey, H. Bolvin, M. Cordonnier, C. Demuyne, J. L. Destombes, R. Escribano and P. C. Gomez, *Can. J. Phys.* **72**, 967 (1994).

^cJ. T. Hougen, *J. Mol. Spectrosc.* **114**, 395 (1985).

^dM. Cordonnier and L. H. Coudert, *J. Mol. Spectrosc.* submitted (1996).

WF07

15 min 3:12

INTERNAL ROTATION IN THE CH_3^+ MOLECULAR ION

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A semirigid bender analysis is performed to calculate the rotation and internal-rotation energy levels of protonated methane in its ground electronic state. The internal rotation is modelled according to a minimum energy pathway fitted through 13 nuclear configurations optimized at the MP2/6-311++G(2df,2p) level of *ab initio* theory. The internal rotation coordinate is chosen as the average of the three dihedral angles between the C-H bonds of the CH_3^+ moiety and the somewhat separated H_2 moiety. The shape of the internal rotation potential, and the geometrical changes occurring as the molecule internally rotates, will be discussed, and their effect on the energy levels will be determined. The importance of other large amplitude internal motions will also be considered.

WF08

15 min 3:29

Observation of Jet-cooled Radical and Ion by Millimeterwave Spectroscopy Combined with Pulsed-jet Expansion and Discharge Nozzle Technique.

Keiichi Tanaka and Keisuke Uemura

Millimeterwave spectrometer combined with a pulsed supersonic jet nozzle and discharge nozzle was devised and applied to observe the absorption spectra of the jet-cooled radicals and ions in the 100- 300 GHz region. Within a cylindrical electrode (1 = 300, and 100 ϕ) as cathode, a pulse jet nozzle attached 1 ϕ tantalum (10 mm long) tube as anode was placed. Sample gas diluted in several atm of Ar to a few % was injected in the cell with repetition rate of 10 - 30 Hz synchronized with discharge pulse. Millimeterwave was focused tightly just below the nozzle by teflon lenses.

So far we observed $J = 3 - 2$ rotational lines of CS ($^1\Sigma^+$) produced by the discharge of CS₂. The sensitivity of the spectrometer is estimated to be $\Delta I/I = 3 \times 10^{-6}$ from the signal to noise ratio of the ³³S isotopic species. We also observed the $N = 1 - 0$ rotational line of the CN ($^2\Sigma^+$) radical, which was split into seven due to fine and hyperfine structures, with S/N ratio of about 30. The $J = 2 - 1$ rotational line of the DCO⁺ ion ($^1\Sigma^+$) was observed with S/N ratio of about 3. The rotational temperature of molecules within discharge is estimated to be a few ten K. The application of this millimeterwave spectrometer for the detection of light unstable molecules, and for the detection of the van der Waals mode transitions of radical cluster is of great interest.

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Intermission

WF09

15 min 4:00

MILLIMETER-WAVE SPECTRUM OF SILENE: H₂CSiH₂

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Silene has been produced in the gas phase by vacuum flash pyrolysis of 5,6-bis(trifluoromethyl)-2-silabicyclo[2.2.2]octa-5,7-diene (SBO) at 600°C^a. Its rotational spectrum corresponding to a slightly asymmetric top was observed in a liquid nitrogen cooled cell when argon was used as carrier gas.

The assignment of H₂CSiH₂ lines has been made by comparing experimental molecular constants with ab initio predicted values from Breidung and Thiel^b. The observation of several lines belonging to the ²⁹Si isotopic species in natural abundance confirmed unambiguously this identification.

This work led to the first high resolution spectroscopic results for silene. Study of different isotopomers is in progress and will give an experimental structure of this compound.

^aG. Maier, G. Mihm, H. P. Reisenauer, Chem. Ber. 117, 2351 (1984)

^bS. Bailleux, M. Bogey, J. Breidung, H. Bürger, R. Fajgar, Y. Liu, J. Pola, M. Senzlober and W. Thiel, J. Am. Chem. Soc., submitted (1996)

WF10

15 min 4:17

DETERMINATION OF THE GEOMETRIC STRUCTURE OF BUTATRIENYLIDENE, H_2CCCC , AND OF THE HYPERFINE STRUCTURE OF PROPYNONYL, $HCCCO$

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The microwave spectra of the $N = 1 - 0$ and $2 - 1$ transitions of six isotopic species of the singlet carbene butatrienylidene (H_2CCCC , $H_2CCC^{13}C$, $H_2CC^{13}CC$, $H_2C^{13}CCC$, $H_2^{13}CCCC$, D_2CCCC) were measured with a Fourier transform microwave spectrometer and the r_0 and r_s structures were determined. Both structures agree well with the calculated *ab initio* structure indicating that the carbon chain backbone is cumulenec. In addition, the two lowest hyperfine split transitions of $HCCCO$ ($N = 1 - 0$ and $2 - 1$) have been measured with a Fourier transform microwave spectrometer. The frequencies, accurate to better than 0.20 km/s, should help guide future searches for interstellar $HCCCO$.

WF11

15 min 4:34

MICROWAVE SPECTROSCOPY OF THE HCCS AND DCCS RADICALS IN THE VIBRONIC EXCITED STATES

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The microwave spectra of the HCCS and DCCS radicals ($X^2\Pi_i$) in both $CCS(\nu_5)$ and $H(D)CC(\nu_4)$ bending vibronic states were observed in the frequency range of 160–400 GHz with a dc discharge of the C_2H_2 (or C_2D_2) and CS_2 gas mixture. The rotational transition series for the vibronic $^2\Delta_{5/2,3/2}(\nu_5)$, μ , $\kappa^2\Sigma(\nu_5)$, $^2\Pi_{3/2}(2\nu_5)$, $^2\Delta_{5/2}(\nu_4)$ and $\mu^2\Sigma(\nu_4)$ states were assigned. The analysis of the effective molecular constants showed that the values of the γ_{eff} constants of the vibronic μ , $\kappa^2\Sigma$ states were different from each other by 2–3 GHz, which could not be explained by the up-to-date Renner-Teller theory for a single bending mode. This abnormal Renner-Teller effect may be understood by a new vibronic interaction theory, which was developed by us to consider the cross vibronic interaction between the two bending modes.

WF12

15 min 4:51

MILLIMETER-WAVE SPECTROSCOPY OF NCS: AN ANALYSIS OF VIBRONIC INTERACTION

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The ground electronic state of NCS radical is a $^2\Pi_i$ state and is isovalent with NCO. While NCO is one of the free radicals that have been studied very extensively in the microwave, millimeter-wave and visible-UV regions, high-resolution investigation of NCS has been relatively sparse. We studied the millimeter-wave spectrum of this radical in the ground vibrational state several years ago, and determined precise set of the molecular constants^a. Since then we extended our measurements to the excited vibrational states, $v_2 = 1$ state in particular. The spectrum was found to be complicated due to large Renner-Teller interaction. The Δ and Σ vibronic states are fitted separately using effective Hamiltonians. A more complete global fit including the $v_2 = 2$ vibronic states is in progress and will be discussed.

WF13

15 min 5:08

FOURIER-TRANSFORM MW SPECTROSCOPY OF THE SH($^2\Pi_i$)-Ar AND SD-Ar RADICAL COMPLEXES

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We have studied the SH($^2\Pi_i$)-Ar and SD-Ar radical complexes with FTMW spectroscopy. The complexes were produced in a supersonic free jet by a pulsed discharge of H₂S or D₂S, which was diluted to 0.35% in Ar with a stagnation pressure of 2 atm. R-branch transitions in the lower spin-orbit component ($\Omega=3/2$) for the linear $^2\Pi_i$ radicals were observed for $J'' = 3/2$ to $J'' = 15/2$ in the 8 - 26 GHz region. The transitions were split into two parity components owing to the parity doubling. Each parity component was split further due to the magnetic hyperfine interaction associated with the H/D nucleus.

Rotational constants for SH-Ar and SD-Ar were determined to be 1569.656(2) and 1567.707(2) MHz respectively. The value for SH-Ar agrees well with that of a previous LIF study.^a From the SH/SD data, it was confirmed that the argon atom is located at the hydrogen side of the SH radical. With an assumption that the S-H bond length is equal to that in the monomer, the H-Ar distance is calculated to be 2.900 Å, which is about 0.1 Å longer than that in OH-Ar. The effective D_J constants of SH-Ar and SD-Ar were found to have negative values of -58.4(7) and -50.7(6) kHz respectively.

^aMin-Chieh Yang, Aldo P. Salzberg, Bor-Chen Chang, Christopher C. Carter, and Terry A. Miller, J.Chem.Phys. **98** (1993) 4301.

WF14

15 min 5:25

The Microwave Spectrum of the Open-Shell Complex NO-HF, C.R. DENNIS, C.J. WHITHAM, B.J. HOWARD, The Physical and Theoretical Chemistry Laboratory South Parks Road, Oxford, OX1 3QZ, England

A detailed study of the complex NO-HF has been carried out using the technique of Fourier Transform Microwave Spectroscopy. There have been in excess of a hundred hyperfine transitions recorded in the region from 7 GHz to 19GHz, originating from the $J=5/2(f)-3/2(f)$, $J=3/2(f)-1/2(f)$, $J=3/2(e)-1/2(e)$ and $J=5/2(e)-3/2(e)$ rotational levels. A previous infrared study¹, provided the rotational constants which facilitated the search in the microwave region. An assignment has been carried out using microwave double resonance to deduce connections between the levels.

The hydrogen bond interaction is sufficiently strong to cause considerable quenching of the NO electronic orbital angular momentum giving rise to a Renner-Teller parameter ϵ_2 and a Zeeman interaction with the Earth's magnetic field. A magnetic interaction has been observed between the unpaired electron on NO and both the hydrogen and fluorine nuclei in the HF.

Initial analysis has shown that the Renner-Teller parameter ϵ_2 has a negative sign, indicating that the unpaired π^* electron prefers to be in the plane of the complex and as a consequence of an attractive interaction to the neighbouring HF.

It is believed that this is the first such observation of a magnetic interaction induced by complexation. Such interactions are extremely sensitive to the nature of the forces between partners in a complex, and should be a common feature of microwave spectra of open-shell complexes involving magnetic nuclei such as hydrogen, nitrogen and fluorine.

WF15

15 min 5:42

LABORATORY SPECTROSCOPY OF THE C_7H AND C_8H RADICALS

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The linear carbon chain radicals C_7H and C_8H have been detected in their $^2\Pi$ electronic ground states in an acetylene/argon discharge. For each radical, both spin-orbit components have been detected, precise values for the rotational, fine structure, and lambda-doubling constants determined, and the entire fine structure-rotational spectrum calculated. The lowest rotational transitions of C_7H and C_8H were also observed in a pulsed discharge supersonic molecular beam source by Fourier transform microwave spectroscopy. A summary of results, including an analysis of the hyperfine structure will be presented.

WG01

15 min 1:30

EXTRAPOLATION OF CARBON DIOXIDE LINE POSITIONS FOR HITEMP
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Simulation of carbon dioxide spectra at temperatures up to 1500K requires higher vibrational levels, and line positions to much higher angular momentum quantum number J , than have been observed. Direct Numerical Diagonalization (DND)¹ allows extrapolation to such high vibrational levels and high J , but does not reproduce observed lower- J line positions to within experimental accuracy.

For the HITEMP line parameter compilation, we chose to fit spectroscopic constants G_v , B_v , D_v , H_v , L_v and P_v to the observed line positions, and to high- J DND-calculated line positions, simultaneously. This allows smooth extrapolation while preserving a good fit to the observed positions. Examples of bands fitted in this way, and the quality of fit to be expected in HITEMP, will be presented.

1. R.B. Wattson and L.S. Rothman, *J. Mol. Spectrosc.* 119, 83 (1986).

WG02

15 min 1:47

An ab initio calculation of BH_2^- rovibronic energies: a very small singlet-triplet splitting

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For each of the \tilde{X}^3B_1 , \tilde{a}^1A_1 , and \tilde{b}^1B_1 electronic states of the BH_2^- molecular ion we have calculated over 50 ab initio points on the potential energy surfaces using the MRD-CI method for all eight electrons. Analytical functions were fitted through the points for each state, and the functions for the \tilde{a} and \tilde{b} states were such that the surfaces remain degenerate at all linear configurations. For the \tilde{X} state the rotation-vibration energies were calculated from the surface using the MORBID^a Hamiltonian, and for the \tilde{a} and \tilde{b} states the rovibronic energies were calculated using the RENNER^b Hamiltonian. For the \tilde{X} state we obtain $r_e = 1.2034 \text{ \AA}$, $\alpha_e = 129.5^\circ$ and a barrier to linearity of 2226 cm^{-1} . The vibrational wavenumbers are determined to be $\nu_1 = 2353 \text{ cm}^{-1}$, $\nu_2 = 883 \text{ cm}^{-1}$ and $\nu_3 = 2498 \text{ cm}^{-1}$. For the \tilde{a} -state we determine $r_e = 1.2369 \text{ \AA}$, $\alpha_e = 105.7^\circ$, a barrier height to linearity of 6071 cm^{-1} and the vibrational wavenumbers $\nu_1 = 2070 \text{ cm}^{-1}$, $\nu_2 = 986 \text{ cm}^{-1}$, and $\nu_3 = 2059 \text{ cm}^{-1}$. For the \tilde{b} -state we determine $r_e = 1.1936 \text{ \AA}$, $\alpha_e = 135.9^\circ$, a barrier height to linearity of 1069 cm^{-1} and the vibrational wavenumbers $\nu_1 = 2399 \text{ cm}^{-1}$, $\nu_2 = 915 \text{ cm}^{-1}$, and $\nu_3 = 2591 \text{ cm}^{-1}$. The most interesting result we obtain is that the singlet-triplet splitting $T_0(\tilde{a}^1A_1)$ is only 153 cm^{-1} for $^{11}BH_2^-$. Hence singlet-triplet perturbations will significantly affect all levels of the ground state.

^aP. JENSEN, *J. Mol. Spectrosc.* 128, 478-501 (1988).

^bP. JENSEN, M. BRUMM, W. P. KRAEMER, AND P. R. BUNKER, *J. Mol. Spectrosc.* 171, 31-57 (1995); M. KOLBUSZEWSKI, P. R. BUNKER, W. P. KRAMER, G. OSMANN, AND P. JENSEN, *Mol. Phys.*, in press.

WG03

15 min 2:04

EXPERIMENTAL AND THEORETICAL STUDIES OF $Mn_2(CO)_{10}$

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Ground state resonance Raman spectroscopy, Fenske-Hall molecular orbital calculations, and density functional theory were utilized to study the photochemistry of $Mn_2(CO)_{10}$ in an attempt to understand better the photochemical reaction pathways of dinuclear transition metal organometallic complexes. In this work, resonance enhancement of the e_g Mn-C-O bending mode, the e_g C-O stretching vibration and the a_1 Mn-Mn bond stretch are found to play an important role in the resonance Raman spectra of $Mn_2(CO)_{10}$. These data, together with the theoretical calculations, are consistent with the proposal that the photochemical intermediate $Mn_2(CO)_9$ contains a linear semi-bridging CO.

WG04**15 min 2:21**

VIBRATIONAL PROPERTIES OF X_3^+ AND X_5^+ ($X=F, Cl, Br, I$) CLUSTERS IN MADELUNG POTENTIALS

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The infrared and Raman spectra of the trihalogen and pentahalogen cations are well known from experiments on crystals containing them as counterions. A proper analysis of the spectra is impossible without taking into account the influence of the crystal field on the cation. In this work, ab initio and density functional calculations have been carried out on the free X_3^+ and X_5^+ ($X=F, Cl, Br, I$) cluster cations. Comparable calculations have been performed on the clusters Cl_3^+ , Br_3^+ , I_3^+ , Br_5^+ , I_5^+ , $I_3Cl_2^+$, and $I_3Br_2^+$ embedded in the point charges derived from the Madelung potentials of the crystal fields. It has been shown that the Madelung potential plays an important role in the vibrational properties of these cations with strong cation-anion interactions. The computed vibrational frequencies, force constants, and infrared intensities are in good agreement with the experimental data.

WG05**15 min 2:38**

TUNNELING SPLITTINGS IN HYDROGEN-BONDED MOLECULES AND HYDROGEN TUNNELING IN CONDENSED PHASES

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A theory of tunneling splitting in hydrogen-bonded systems and hydrogen tunneling dynamics in condensed phases is presented. The theory is developed on a model of a fast-moving particle in an one-dimensional metastable or bistable potential coupled to a bath of lower-frequency harmonic oscillators. A power series expansion of the coupling terms up to a biquadratic one is included explicitly which accounts for all different coupling symmetries in the system. Analytical formulae are derived for the tunneling splitting or tunneling rate in terms of the normal modes of the system making the treatment applicable to systems of arbitrary size. For vibrational eigenvalue problems the treatment can be viewed as an extension of the normal mode treatment to incorporate small tunneling splittings. For dynamical problems, such as hydrogen-transfer reactions and hydrogen diffusion in solids or at surfaces, the method incorporates a precise definition of a transition state and can be viewed as a close quantum-mechanical analog of the classical transition-state theory. The method is tested on model multidimensional tunneling problems against numerical calculations from the literature with excellent results. Applications to calculations of tunneling splittings and isotope effects in hydrogen-bonded molecular systems and comparisons with experimental data are given.

WG06

10 min 2:55

ANALYTICAL APPROXIMATION FOR ADIABATIC AND NONADIABATIC ELECTRONIC MATRIX ELEMENTS OF HOMONUCLEAR DIATOMIC RYDBERG STATES. APPLICATION TO SINGLET P-COMPLEX OF HYDROGEN MOLECULE

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Based on the one-channel quantum defect theory (QDT) representation of Rydberg electronic states of homonuclear diatomic molecule estimated at the standard Born-Oppenheimer approximation the simple analytical expressions to approximate adiabatic and nonadiabatic electronic matrix elements have been offered. The relations for matrix elements of radial coupling operator (first and second partial derivatives on internuclear distance R) have been obtained by applying the both diagonal and nondiagonal forms of Hellman-Feynman theorem as well as well-known scaled property of Coulomb functions at a small distance from a core r . The matrix elements of electronic coupling operator have been found in closed form based on the results of the hypervirial theorem as well as the Sidis equation. Using semiclassical approximation of QDT function formulae for integrals $\langle \nu_i | r^k | \nu_j \rangle$, where $k = 0, 2$ have been developed. It allowed for to find R -dependence matrix elements of both l and electronic coupling in an analytical form as well. The formulae have been tested on low-lying states of singlet p-complex of molecular hydrogen by comparison with "exact" ab initio results.

Intermission

WG07

15 min 3:20

AN EMPIRICAL MODEL FOR THE INFRARED COLLISION INDUCED ABSORPTION BAND OF N_2 NEAR $4.3 \mu m$,
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Very accurate measurements of collision induced absorption by pure nitrogen have been made in the 0 - 10 atm and 230 - 300K pressure and temperature ranges, respectively, using a BOMEM Fourier transform spectrometer with a resolution of 0.5 cm^{-1} . The measurements are, in general, in good agreement with those reported previously but are more precise. Small weak features have been found superimposed on the broad N_2 continuum which previously had been observed only at very low temperatures. These features have negligible temperature dependence and, at this time, their origin is not known. Available data in the range of temperature from 190 to 300K have been used to derive a simple empirical model suitable for calculating atmospheric absorption. Assuming an atmospheric composition of 21% O_2 + 79% N_2 , the absorption coefficient of N_2 in the atmosphere can be expressed as:

$$\alpha_{N_2}^{atm}(\sigma, P, T) = \left[P \frac{273}{T} \right]^2 \left[0.8387 - 0.0754 \frac{T}{T_0} \right] B_{N_2-N_2}^0(\sigma) \exp \left[\beta_{N_2-N_2}^0(\sigma) \left(\frac{1}{T_0} - \frac{1}{T} \right) \right]$$

where the reference temperature, T_0 , is 296K and $B_{N_2-N_2}^0(\sigma)$ and $\beta_{N_2-N_2}^0(\sigma)$ are empirical fitting parameters.

WG08

15 min 3:37

VIBRATIONAL DEPENDENCE OF HYDROGEN-BROADENED HALFWIDTHS OF WATER VAPOR TRANSITIONS

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The pressure broadened halfwidth of water vapor transitions in the ground, ν_2 , ν_1 , and ν_3 bands are calculated with hydrogen as the perturbing species using the fully complex Robert and Bonamy theory.^{a b} The assumed intermolecular potential is a combination of electrostatic, Lennard-Jones 6-12 atom-atom (expanded to 4th order), induction, and dispersion terms. The results are compared with the measurements of Brown and Plymate^c and the vibrational dependence of the halfwidths investigated.

^aD. Robert and J. Bonamy, "Short range force effects in semiclassical molecular line broadening calculations", *J. Phys.* (Paris) 40,923 (1979).

^bR. Lynch, R. R. Gamache, and S. P. Neshyba, "Fully Complex Implementation of the Robert-Bonamy Formalism: Halfwidths and Line Shifts of H₂O Broadened by N₂," submitted to *J. Chem. Phys.* November, 1995.

^cL. R. Brown and C. Plymate, in press, *JQSRT* (1996).

WG09

15 min 3:54

HALFWIDTHS AND LINE SHIFTS OF H₂O TRANSITIONS BROADENED BY CO₂

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The complex semiclassical formalism of Robert and Bonamy^{ab} is used to calculate both halfwidths and line shifts for water vapor in a bath of carbon dioxide gas. The assumed intermolecular potential is a combination of electrostatic, Lennard-Jones 6-12 atom-atom (expanded to 8th order), induction, and dispersion terms. Calculations are made for transitions in the ν_1 , $2\nu_2$, and ν_3 vibrational band and are compared with the measurements of Gamache et al.^c Good agreement with the experimental results is observed for both the halfwidth and line shifts. It is shown that the imaginary parts are important for both the line shift and halfwidth calculations.

^aD. Robert and J. Bonamy, "Short range force effects in semiclassical molecular line broadening calculations", *J. Phys.* (Paris) 40, 923 (1979).

^bR. Lynch, R. R. Gamache, and S. P. Neshyba, "Fully Complex Implementation of the Robert-Bonamy Formalism: Halfwidths and Line Shifts of H₂O Broadened by N₂," submitted to *J. Chem. Phys.* November, 1995.

^cR. R. Gamache, S. P. Neshyba, J. J. Plateaux, A. Barbe, L. Rgalia, and J. B. Pollack, *J. Mol. Spectrosc.* 170, 131 (1995).

WG10

15 min 4:11

ANALYSIS OF THE LINE POSITIONS AND LINE INTENSITIES IN THE ν_2 BAND OF THE WATER MOLECULE

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The somewhat successful treatment developed to account for the anomalous centrifugal distortion displayed by the water molecule^a has been slightly altered in order to permit a calculation of the rotational energy in the ground and in the $\nu_2 = 1$ vibrational states using the *same* set of spectroscopic constants. This new treatment has been used to carry out two analyses of large bodies of data relevant to the water molecule. In the first analysis, in addition to the rotational levels of the ground^b and $\nu_2 = 1$ ^c vibrational states, infrared and microwave transitions within the ground and the $\nu_2 = 1$ vibrational states as well as infrared transitions belonging to the ν_2 band^d were considered. The unitless standard deviation of this first analysis is 1.4, the maximum J - and K_a -values considered being 25 and 20, respectively, and 71 spectroscopic constants were used. In the second analysis, the intensities published by Toth^d were included in a least squares fit procedure in which line-strengths were evaluated choosing a physically reasonable dipole moment function and computing its matrix elements with the spectroscopic constants of the first analysis.

In the paper, the results obtained in the two analyses will be presented. The potential energy and dipole moment functions derived from the analyses will be discussed. The latter function will be compared to that obtained by other authors^e.

^aL. H. Coudert, *J. Mol. Spectrosc.* **165**, 406 (1994).

^bJ.-M. Flaud, C. Camy-Peyret, and J. P. Maillard, *Mol. Phys.* **32**, 499 (1976).

^cC. Camy-Peyret, J.-M. Flaud, J. P. Maillard, and G. Guelachvili, *Mol. Phys.* **33**, 1641 (1977).

^dR. A. Toth, *J. Opt. Soc. Am. B* **11**, 2236 (1991).

^ePer Jensen, S. A. Tashkun, and V. I. Tyuterev, *J. Mol. Spectrosc.* **168**, 271 (1994).

WG11

10 min 4:28

MODELING OF THE FUNDAMENTAL RAMAN AND INFRARED CH STRETCHING SPECTRA OF CHD₂ PICOLINES

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The quasi-free internal rotation of the methyl group in the α , β and γ CHD₂ picolines leads to complex features observed in the Raman and infrared CH stretching spectra. A quantum theory has been developed to model these spectra, taking explicitly into account the coupling between the slow internal motion and the much faster CH stretching vibration.

In the ground vibrational state ($v=0$), the effective potential of internal rotation is calculated by adding to the methyl rotation potential energy, the variation of the zero point vibrational energy during the internal motion, determined by ab-initio.

In the CH stretching excited state, this effective potential is added to the CH stretching vibrational contribution, determined from the conformational dependence of the CH bond length.

The CH transitions between the effective potentials in the ground ($v=0$) and the first excited ($v=1$) CH stretching states are then calculated to reconstruct the fundamental Raman and IR spectra. The Raman intensities are determined from simple Franck-Condon factors, and the IR intensities are calculated from dipole moment derivatives determined by ab-initio. The so calculated spectra agree well with the experimental ones.

WG12

15 min 4:40

ON THE POSSIBILITY OF ESTIMATION HARMONIC FREQUENCIES OF MOLECULES
(INTRAMOLECULAR FORCE FIELD PARAMETERS) ON THE BASE OF INFORMATION
ABOUT ITS PURE ROTATIONAL SPECTRUM

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In the process of study near local mode XY_2 and XY_3 molecules we found^a that all properties of spectroscopic parameters of such type molecules are determined, considerably, by the simplest solutions of equations, which connect ambiguous parameters $\sin \gamma_i$ with the parameters of intramolecular potential function and masses of molecular nucleus. As the analysis of other solutions of above mentioned equations shown, simple (nondepended on intramolecular force constants) results for $\sin \gamma_i$ parameters can be obtained in general enough case (with only one limitation $m/M \ll 1$) for XY_2 and XY_3 molecules. On this base it is shown that for molecules of such types experimental information on rotational and quartic centrifugal distortion parameters (e.g., determined from microwave spectra) allows one to predict with high enough accuracy harmonic frequencies and quadratic force constants of intramolecular potential function even without any additional information about fundamental or overtone bands. Calculations for different real molecules are presented, as an illustration. Attempt of expansion of results to more complicated molecular systems is discussed.

Part of this work was supported by Russian Foundation on Fundamental Researches (Pr.N94-02-03081a).

^aO.N.Ulenikov and R.N.Tolchenov, Abstr.XIV Colloq.High Resolution Molecular Spectroscopy, F23, Dijon (France), 1995.

WG13

15 min 4:57

CALCULATION OF THE SPECIFIC HEAT FROM THE RAMAN FREQUENCY DATA FOR
 NH_4Br , H. YURTSEVEN, Department of Physics, Istanbul Technical
University, Maslak, Istanbul, TURKEY.

We have calculated the specific heat C_v for NH_4Br near its λ -phase transition using our Raman frequency data of the $\nu_{5L0\Gamma}$ (177 cm^{-1}) phonon mode of this crystal. For the C_v calculation we have used an Ising model superimposed on an Einstein and/or Debye model. The specific heat C_{VL} due to the lattice vibrations (Einstein model) and C_{VI} due to the spin interactions (Ising model) were calculated according to $C_v = C_{VL} + C_{VI}$ at various temperatures using our observed Raman frequencies for the 177 cm^{-1} mode of NH_4Br . From our analysis it is concluded that an Ising model superimposed on an Einstein and/or Debye model explains adequately the observed behaviour in the lattice region of the NH_4Br crystal.

WG14

15 min 5:14

PRECISE STUDY OF CHD₃ SPECTRUM IN THE REGION OF 1900-2800 CM⁻¹

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High resolution spectrum of CHD₃ (instrumental resolution 0.0035 cm⁻¹) was recorded on the Bruker IFS 120HR Fourier transform spectrometer (Oulu) and analyzed in the region of 1900-2800 cm⁻¹. Spectrum in this region contains two strong fundamental bands $\nu_2(A_1)$ and $\nu_4(E)$, and some weak combination and overtone bands $2\nu_3(A_1)$, $\nu_3 + \nu_6(E)$, $2\nu_6(A_1)$, $2\nu_6(E)$, $\nu_3 + \nu_5(E)$, $\nu_5 + \nu_6(A_1)$, $\nu_5 + \nu_6(E)$, $2\nu_5(A_1)$, and $2\nu_5(E)$. There are only few detailed studies of spectrum in this region^{a-d}. However, even at the recent paper (d) parameters were not determined which would reproduce initial experimental data with satisfactory accuracies. We used for analysis specially derived model of Hamiltonian which based on the irreducible tensorial sets theory. Taking into account a). higher-order resonance interactions between above mentioned vibration-rotation bands and b). higher-order splitting parameters we obtained set of spectroscopic constants which reproduce initial experimental data with the accuracies near to experimental uncertainties. Anomalous behaviour of A_1-A_2 splittings in E -type vibrational states and anomalous shifts of energy levels in A_1 -type vibrational states are discussed. Part of this work was supported by Russian Foundation on Fundamental Researches (Pr.N95-03-08081a).

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WG15

15 min 5:31

Ab initio study of a quasi van der Waals molecule: N₂O₄.

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A critical review of the *ab initio* literature on the ground electronic state of N₂O₄ is presented. It is completed by new calculations including higher order electron correlation effects using the MP4 and internally-contracted MRCI methods and some open questions are revisited. They concern the harmonic and anharmonic force fields, the torsional energy barrier, the dissociation path into two NO₂ radicals and the assignment of the IR spectrum. Most properties affected by the quasi van der Waals nature of the NN bond are shown to require a high level of theory (MRCI/cc-pVTZ). Reliable harmonic vibrational frequencies (within 3%) are however obtained from the MP4/6-31G* method. This level has been adopted to calculate the IR spectrum from anharmonic variational calculations within a 4 dimensional effective model. An unambiguous assignment of the experimental spectrum^a below 600 cm⁻¹ is proposed.

^aJ. Koput, J.W.G. Seibert and B.P. Winnewisser, *Chem. Phys. Lett.*, **204**, 183 (1993).

WG16

10 min 5:48

Line-mixing effects in Σ - Π Q-branches of CO_2 . Temperature, pressure, and perturber dependencies, R. Rodrigues,¹ B. Khalil,² R. Le Doucen,² J.M. Hartmann,¹ and L. Bonamy.³

Line-mixing effects in two infrared CO_2 Q-branches of Σ - Π vibrational symmetry near 15 μm mixed with He, Ar, N_2 and O_2 have been studied over a wide range of temperature (200–300 K) and pressure (0.5–10 bars). A full analysis of the perturbers influence on line-mixing within the Q-branch has been made using the recent formalism developed by L. Bonamy⁴ and al. accounting for the rotational angular momentum relaxation mechanism. The correct agreements obtained in spectra computations show the validity of the model.

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⁴ L. Bonamy and F. Emond, "Rotational-angular-momentum relaxation mechanisms in the energy-corrected-sudden scaling theory", *Phys. Rev. A* 51, 1235-1240 (1995).

WH01

15 min 1:30

ON THE LONG RANGE PART OF THE POTENTIAL CURVE OF THE $A^1\Sigma_u^+$ STATE IN ${}^6\text{Li}_2$,
F. MARTIN, M. AUBERT-FRECON, R. BACIS, A.J. ROSS, P. CROZET, I. RUSSIER, S. MAGNIER,
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NB, Canada, E3B 5A3.

Using results from photoassociation experiments involving ultracold ${}^6\text{Li}$ atoms [1] and dispersed fluorescence data from optical-optical double resonance spectroscopy [2], we have constructed an experimental RKR curve for the $A^1\Sigma_u^+$ state extending to 74 Å. The dissociation energy D_e with respect to the bottom of the $A^1\Sigma_u^+$ state is obtained directly from a fit of the energy levels, $D_e = 9352.03(1) \text{ cm}^{-1}$. The potential energy curve $V(R)$ for the $A^1\Sigma_u^+$ state deviates slowly from the usual $V(R) = D_e - C_3/R^3 + \dots$ expression [3], reflecting a gradual transition from Hund's case a) to Hund's case c) coupling in the molecule. The outer limb of the curve varies with $1/R^n$ in a more complex way because of interactions between the two 0_u^+ components dissociating to $\text{Li}(2s) + \text{Li}(2p)$.

We present the general analytical form of the long-range part of the $A^1\Sigma_u^+$ state derived from a treatment which includes all the off-diagonal terms in the interaction matrix. The lithium dimer data have provided a test of the validity of this model; energies are recalculated to within 0.008 cm^{-1} for $12 \leq R \leq 74 \text{ Å}$, with six parameters.

[1] Abraham et al., J. Chem. Phys. **103**, 773 (1995).

[2] Linton et al., J. Mol. Spec. **00**, 00 (1996).

[3] LeRoy, J. Chem. Phys. **73**, 6003 (1980).

WH02

15 min 1:47

ON THE $b^3\Pi_u$ STATE OF ${}^7\text{Li}_2$, I. RUSSIER, A. YIANNPOULOU, A.J. ROSS, F. MARTIN,
P. CROZET, R. BACIS, S. CHURASSY, Laboratoire de Spectrométrie Ionique et Moléculaire, UMR 5579
CNRS et Université Lyon I, Bât 205 Campus La Doua, 69622 Villeurbanne Cedex, France; C. LINTON,
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The $(1)b^3\Pi_u$ state of ${}^7\text{Li}_2$ has been investigated by using two different optical-optical double resonance mechanisms with single mode dye lasers.

1) Perturbation facilitated optical-optical double resonance

Using established "gateways" to the triplet manifold in ${}^7\text{Li}_2$ [1], it is possible to reach many vibrational levels of the $(2) {}^3\Delta_g$ and $(1) {}^3\Delta_g$ Rydberg states with R6G plus DCM or LD700 dyes. The range of N' is very limited because of the restricted access to the triplet systems. Direct fluorescence from these levels to vibrational levels $1 \leq v'' \leq 27$ in the $b^3\Pi_u$ state were recorded at 0.07 cm^{-1} resolution on a Fourier transform spectrometer.

2) Optical-optical double resonance within the singlet manifold, followed by collisionally induced fluorescence.

When levels $v=2$ and 3 of the $F^1\Sigma_g^+$ state were excited, collisional processes resulted in efficient energy transfer to the $(1) {}^3\Delta_g$ state. Rotational levels $N' \leq 20$ were observed in the levels $v'=0, 1$ and 2 of $(1) {}^3\Delta_g$. Bands of the $(1) {}^3\Delta_g \rightarrow (1) b^3\Pi_u$ system with $0 \leq v'' \leq 7$ were recorded on the Fourier transform spectrometer at a resolution of 0.07 cm^{-1} . Their structure clearly reveals the effects of interaction between the $b^3\Pi_u$ state and the repulsive inner wall of the $a^3\Sigma_u^+$ state, as alternate rotational levels are shifted and broadened by predissociation.

Combining the data from both experiments, we have derived an RKR curve for the $b^3\Pi_u$ state up to $v=27$ (which covers about 65% of the total well depth), and have studied the shifts caused by predissociation as a function of v'' and N'' . These are compared with those observed in the past for the ${}^6\text{Li}_2$ molecule [2], and the results will be discussed.

[1] Li Li et al., J. Chem. Phys. **96**, 3342 (1992)

[2] Schmidt et al., Chem. Phys. Lett. **143**, 353 (1988), Linton et al., J. Mol. Spec. **151**, 159 (1992).

WH03

15 min 2:04

MULTIPLE RESONANCE SPECTROSCOPY OF THE $G^1\Pi_g$ AND $F^1\Sigma_g^+$ STATES OF $^7\text{Li}_2$: DETECTION OF PREDISSOCIATING $F^1\Sigma_g^+$ STATE LEVELS THROUGH ATOMIC SIDE FLUORESCENCE, S. ANTONOVA, K. URBANSKI, A. M. LYYRA, Physics Department, Temple University, Philadelphia, Pa 19122, LI LI, Department of Modern Applied Physics, Tsinghua University, Beijing.

Optical-Optical Double Resonance (OODR) was employed to excite ro-vibrational levels in the unknown upper portions of the $G(1)^1\Pi_g$ and $F(4)^1\Sigma_g^+$ states. Although both are singlet states and dissociate to the same atomic limit ($2p+2p$) they behave in significantly different ways. Vibrational levels as high as $v = 48$, which has rotationless energy within 1% from the dissociation energy, were observed in the $G^1\Pi_g$ state by detecting molecular fluorescence. In the $F^1\Sigma_g^+$ state all levels in the energy region above the $2s+3s$ atomic limit were found to be strongly predissociated. This is due to interactions with the continuum of the $E^1\Sigma_g^+$ state which at long internuclear distance dissociates to the $2s + 3s$ atomic limit. Because of the very short lifetimes these levels were detected using atomic side fluorescence.

A C_5 coefficient was determined from the last few outer turning points of the experimental RKR potential curve of the $G^1\Pi_g$ state. Rotational and vibrational dependence of the line width for the predissociated $F^1\Sigma_g^+$ state levels was investigated and a preliminary RKR curve which covers 99.6% of the potential well has been derived from experimental data.

WH04

15 min 2:21

COLLISIONAL TRANSFER AND GATEWAY EFFECT IN SINGLE AND DOUBLY EXCITED STATES OF Li_2 . S. ANTONOVA, K. URBANSKI, J. QI, A.M. LYYRA, Physics Department, Temple University, Philadelphia, Pa 19122, LI LI, Department of Modern Applied Physics, Tsinghua University, Beijing.

We have studied in a series of experiments the state-to-state collision propensity rules in both $^7\text{Li}_2$ and $^6\text{Li}^7\text{Li}$ dimers. A breakdown of the symmetric \neq antisymmetric (s \neq a) rotational level selection rule was observed for collisional population transfer for the nearly homonuclear $^6\text{Li}^7\text{Li}$ molecule, but no s \rightarrow a radiative transitions were detected.

We have also studied the role of perturbations in collisional population transfer between excited singlet and triplet states, known as the gateway effect. Either the $F^1\Sigma_g^+$ or the $G^1\Pi_g$ state is populated by Optical-Optical Double Resonance and the subsequent fluorescence to a lower triplet state is resolved. Singlet-triplet gateways are identified and found to be the principal mechanism for the well known collision-induced side fluorescence detection method.

WH05

15 min 2:38

LOW-BARRIER ROTATION-PSEUDOROTATION HAMILTONIAN AND APPLICATION TO THE B STATE OF Na_3 , NOBUKIMI OHASHI AND MAKIKO TSUURA, Department of Physics, Faculty of Science, Kanazawa University, Kakuma, Kanazawa, Japan 920-11; JON T. HOUGEN, Molecular Physics Division, National Institute of Standards and Technology, Gaithersburg, MD 20899; WOLFGANG E. ERNST, Department of Physics, The Pennsylvania State University, 104 Davey Laboratory, University Park, PA 16802; AND STEFAN RAKOWSKY, Max-Planck-Institut für Strömungsforschung, Bunsenstr. 10, D-37073 Göttingen, Germany

A formalism has been developed for treating the rotation-pseudorotation problem in Na_3 molecules which has many analogies with, but is not identical to, the traditional principal axis formalism for methyl-top internal rotor molecules. The pseudorotational coordinate (angle) χ_p and D_{3h} group theory are taken from our previously developed high barrier formalism¹, and lead to a molecular Hamiltonian containing the following terms (up to second order)

$$H = F\chi_p^2 + \frac{1}{2}V_3(1 - \cos 3\chi_p) + BJ^2 + (C-B)J_z^2 + Q\chi_p J_z + f_+ J_+^2 + f_- J_-^2.$$

The first two terms (F, V_3) represent the three-identical-well particle-on-a-ring pseudo-rotational problem. The next two terms (B, C) represent an oblate symmetric top rotational Hamiltonian (z axis perpendicular to the Na_3 plane). The fifth term (Q) represents the Coriolis interaction between the pseudo-rotational and overall-rotational angular momentum. Up to this point the Hamiltonian can be mapped onto that for methyl-group internal rotation in an oblate symmetric top. The final two terms are peculiar to the present problem. They contain products of the rotational angular momentum ladder operators $J_{\pm} = J_x \pm iJ_y$ and coefficients f_{\pm} , which unlike the coefficients F, V_3, B, C, Q above cannot be constants, but must be expressed as a Fourier series in the pseudorotation functions $\exp(im\chi_p)$, where $m = +1 \text{ mod } 3$. These final two terms allow for "rotation" of the asymmetric rotor A, B, C axes when pseudorotation occurs and each of the Na atoms in turn occupies the apex position in the distorted triangle equilibrium structure. As might be expected, they are responsible for a number of unusual features in the rotational energy level pattern.

Various aspects of the energy levels arising from this Hamiltonian when the barrier $V_3 = 0$ will be discussed, as well as a relatively successful fit of published² and unpublished measurements from earlier B-X pump-probe experiments.

¹N. Ohashi, M. Tsuura and J. T. Hougen, *J. Mol. Spectrosc.* **173**, 79-99 (1995).

²W. E. Ernst and S. Rakowsky, *Can. J. Phys.* **72**, 1307-1314 (1994).

WH06

15 min 2:55

OPTICAL-OPTICAL DOUBLE RESONANCE SPECTROSCOPY OF THE A-X AND B-X SYSTEMS OF Na_3 , DAVID T. VITUCCIO, OLEG GOLONZKA, and WOLFGANG E. ERNST, Department of Physics, The Pennsylvania State University, University Park, PA 16802.

In the B state of Na_3 , the three sodium nuclei can perform an almost free pseudorotational motion in the molecular plane. This purely vibrational movement is characterized by quantum numbers u (denoting the radial displacement amplitude) and j (the vibronic angular momentum). Recent work from this lab has shown that for $j > 0$, each rotational level in the B state splits into two Coriolis components. Furthermore, this study indicates that the vibronic angular momentum is integer quantized¹. The corresponding rotational analysis was based on a simple model assuming well separated vibronic bands--as is the case for $u \geq 1$ --and rotational quantum numbers $J \leq 13$.

This talk reports new optical-optical double resonance experiments in which the frequency of the labeling laser was tuned to a transition in the A-X system--previously investigated by the groups of Demtröder³ and Tiemann⁴. A second laser was scanned across the $u=0$ and 1, $j=0, 1, 2$, and 3 vibronic bands in the B-X system. Such a technique gives a greatly improved signal to noise ratio in comparison with our earlier studies in which labeling was done in the B state. The previously unrecorded $u=0$ spectrum is of particular theoretical interest because the $j=0$ and 1 sublevels lie somewhat closer together than the corresponding pairs in $u \geq 1$ states suggesting that these levels lie near (or even below) the pseudorotational barrier. Efforts are underway to determine the height of the barrier from an analysis of the $u=0$ spectrum.

¹W.E. Ernst and S. Rakowsky, *Phys. Rev. Lett.* **74**, 58 (1995).

²W.E. Ernst and S. Rakowsky, *Ber. Bunsenges. Phys. Chem.* **99**, 441 (1995).

³H.-A. Eckel, J.M. Gress, J. Biele, and W. Demtröder, *J. Chem. Phys.* **98**, 135 (1993).

⁴M. Meyer zur Heide, E. Tiemann, and D. Wendlandt, *Chem. Phys. Lett.* **199**, 590 (1992).

WH07

15 min 3:12

GLOBAL FIT OF THE B-X SYSTEM OF Na₃ USING A NEW MODEL HAMILTONIAN

OLEG GOLONZKA, DAVID T. VITUCCIO, and WOLFGANG E. ERNST,

Department of Physics, The Pennsylvania State University, University Park, PA 16802.

The A and X states of Na₃ can be thought of as ordinary asymmetric rotors (complicated slightly by spin-rotation interaction) but the B state must be treated as a floppy molecule since it exhibits an almost free pseudorotational motion^{1,2}. Because of the peculiar nature of the centrifugal distortion in the B state, previous fitting of the B-X system has been most successful for P and R type transitions involving ground state levels characterized by J, K_a, K_c = J, 0, J or J, 1, J-1, i.e., levels with J-K_c = 0 or 1.

The present talk will describe our progress in globally fitting recently recorded³ transitions involving levels with J-K_c > 1 in order to more thoroughly test the correctness of the recently developed model Hamiltonian². In addition, our experiments have revealed an unexpected splitting of each Coriolis component in pseudorotational states with angular momentum quantum number j ≥ 1. This small splitting--like the larger Coriolis splitting itself--is approximately proportional to j⁴. We believe it arises from some type of interaction between the electron spin angular momentum and the pseudorotational angular momentum. Our attempts to describe this phenomenon will also be discussed.

¹N. Ohashi, M. Tsuura, and J.T. Hougen, *J. Mol. Spectrosc.* 173, 79 (1995).

²N. Ohashi, M. Tsuura, J.T. Hougen, W.E. Ernst, and S. Rakowsky, this conference.

³D.T. Vituccio, O. Golonzka, and W.E. Ernst, this conference.

⁴W.E. Ernst and S. Rakowsky, *Phys. Rev. Lett.* 74, 58 (1995).

Intermission

WH08

15 min 3:45

OPTICAL SINGLET AND TRIPLET BANDS OF HOMONUCLEAR ALKALI DIATOMICS ATTACHED TO COLD HELIUM CLUSTERS.

J. HIGGINS, C. CALLEGARI, J. REHO, W.E. ERNST, AND G. SCOLES, Department of Chemistry, Princeton University, Princeton, NJ 08544

Large helium clusters consisting of several thousand atoms are produced in a supersonic expansion and doped with alkali atoms in a low pressure pick-up scattering cell. Laser-induced fluorescence spectroscopy is used to probe the influence of the cold He environment (internal temperature of 0.4K) on the formation and spectra of alkali molecules. Here, we will report our measurements on the homonuclear diatomics Li₂, Na₂, and K₂.

As published earlier^{1,2}, weakly bound states can be formed due to the low temperature. We have recorded both laser excitation spectra and spectrally resolved emission for the $1^3\Pi_g - 1^3\Sigma_u^+$ transition of Li₂ and K₂ as well as for the $1^3\Sigma_g^+ - 1^3\Sigma_u^+$ transition of Na₂. The triplet transitions in Li₂ and in K₂ had not been directly observed so far. In the case of Li₂, the upper state potential is weakly repulsive and, for K₂, the $1^3\Pi_g$ state has a shallow well with a barrier towards dissociation. After excitation of this state, the spectrally resolved fluorescence reveals the atomic K (4p -4s) transition is the strongest decay channel, while also the K₂ $B^1\Pi_u - X^1\Sigma_g^+$ and $1^3\Pi_g - 1^3\Sigma_u^+$ emission are observed.

Singlet $A^1\Sigma_u^+ - X^1\Sigma_g^+$ transitions have been recorded for Na₂ and K₂. The vibrational bands consist of distinct, narrow zero-phonon lines, a narrow gap, and a wide phonon wing towards the blue. The dynamics of the alkali dimer-He cluster interaction will be discussed.

¹F. Stienkemeier, J. Higgins, W.E. Ernst, and G. Scoles, *Phys. Rev. Lett.* 74, 3592 (1995).

²F. Stienkemeier, W.E. Ernst, J. Higgins, and G. Scoles, *J. Chem. Phys.* 102, 615 (1995).

WH09

15 min 4:02

OBSERVATION OF THE $2^3\Sigma_g^+ - 1^3\Sigma_u^+$ and $1^3\Pi_g - 1^3\Sigma_u^+$ TRANSITIONS OF THE TRIPLET NaK MOLECULE ON THE SURFACE OF HELIUM CLUSTERS

J. HIGGINS, C. CALLEGARI, J. REHO, W.E. ERNST, K.K. LEHMANN, AND G. SCOLES, Department of Chemistry, Princeton University, Princeton, NJ 08544.

High spin (triplet) NaK dimers have been successfully prepared on the surface of helium clusters through a pick-up process in which a He cluster beam passes through two independent alkali pick-up cells, each containing an alkali vapor at pressures around 10^{-2} Pa. Excitation and emission spectra have been recorded for both the $2^3\Sigma_g^+ - 1^3\Sigma_u^+$ and $1^3\Pi_g - 1^3\Sigma_u^+$ transitions. Comparisons of the experimental spectra with the theoretical calculations of Stevens et al.¹ and of Jeung et al.² have been made obtaining information on the potential of the upper $1^3\Pi_g$ state. Similar comparisons with the work of Kowalczyk et al.³ have been made for the $2^3\Sigma_g^+ - 1^3\Sigma_u^+$ transition.

Several different emission channels have been detected for each system following excitation, including atomic fluorescence and non-adiabatic crossings into the singlet manifold of the dimer. The emission spectra provide evidence of vibrational relaxation of the dimer on the He surface occurring on a time scale shorter than that of the molecular fluorescence.

¹ W.J. Stevens, D.D. Konowalow, and Lyn B. Ratchiff, *J. Chem. Phys.* **80**, 1215 (1984).

² G.H. Jeung, J.P. Daudey, and J.P. Malrieu, *Chem. Phys. Lett.* **94**, 300 (1983).

³ W.P. Kowalczyk and N. Sadeghi, *J. Chem. Phys.* **102**, 8321 (1995).

WH10

15 min 4:19

DISPERSED FLUORESCENCE STUDIES OF QUARTET STATE ALKALI TRIMERS

J. HIGGINS, C. CALLEGARI, J. REHO, W.E. ERNST, K.K. LEHMANN, AND G. SCOLES, Department of Chemistry, Princeton University, Princeton, NJ 08544; F. STIENKEMEIER, Fakultät für Physik, Universität Bielefeld, Universitätsstr. 25, D-33615 Bielefeld, Germany; M. GUTOWSKI, Department of Chemistry, University of Gdansk, 80-952 Gdansk, Poland.

The high spin states of Na_3 and K_3 can be formed on the surface of large helium clusters by the aggregation of three alkali atoms with parallel electron spins. The emission spectrum of the $2^4E' - 1^4A'_2$ transition of Na_3 reveals that a non-adiabatic spin flip process occurs in the excited state that leads to an intersystem crossing into the doublet manifold of the trimer. A total of three channels of fluorescence are observed in both Na_3 and K_3 : a) direct emission to the lowest quartet state of the trimer, b) $n^2P_{3/2,1/2} - n^2S_{1/2}$ atomic fluorescence, and c) fluorescence from the singlet dimer $(B)1^1\Pi_u - (X)1^1\Sigma_g^+$ transition. The latter two correspond to the emission of the dissociation products of the doublet trimer after curve crossing. Vibrational analysis of the lowest quartet state of Na_3 provides spectroscopic data with which to test *ab-initio* potential surfaces. The study of the quartet state trimers provides information on the three-body component of the intermolecular energy in these van der Waals molecules. The possibility for time resolved dynamical studies of this simple unimolecular reaction will also be discussed.

WH11

15 min 4:36

VIBRATIONALLY RESOLVED NEGATIVE ION PHOTOELECTRON SPECTROSCOPIC STUDIES OF BARE TRANSITION METAL TRIMERS, S. ALEX, S. M. E. GREEN AND D. G. LEOPOLD, Department of Chemistry, University of Minnesota, Minneapolis MN 55455.

We report the 488 nm negative ion photoelectron spectra of the first row transition metal trimers Cr_3^- , V_3^- and V_2Ni^- , which were prepared in a liquid nitrogen cooled flowing afterglow ion source. The photoelectron transitions to the lowest observed electronic states of Cr_3 , V_3 and V_2Ni , which are assumed to be their ground states, each show two active vibrational modes with frequencies ($\pm 15 \text{ cm}^{-1}$) in the neutral clusters of 465 and 135 cm^{-1} (Cr_3), 470 and 205 cm^{-1} (V_3), and 415 and 250 cm^{-1} (V_2Ni). For the homonuclear trimers, these are assigned as the totally symmetric stretching and bending modes, respectively, of C_{2v} structures. In the mixed early-late transition metal cluster V_2Ni , the higher frequency mode may involve primarily V-V stretching and the lower one Ni-V₂ stretching and/or bending. For all three systems, a comparison of the observed stretching frequencies to those of Cr_2 (452 cm^{-1}) and V_2 (530 cm^{-1}), which have formal bond orders of 6 and 5, respectively, suggest that the triatomic clusters also contain multiple Cr-Cr or V-V bonds. A transition to an excited electronic state of Cr_3 lying $2850 \pm 20 \text{ cm}^{-1}$ above its ground state is also observed, accompanied by a long vibrational progression in a (presumably bending) mode with a neutral molecule frequency of $170 \pm 15 \text{ cm}^{-1}$ in this state. The electron affinities of Cr_3 , V_3 and V_2Ni are determined to be 1.389, 1.103 and $1.112 (\pm 0.006) \text{ eV}$, respectively.

WH12

15 min 4:53

VIBRATIONALLY RESOLVED NEGATIVE ION PHOTOELECTRON SPECTROSCOPIC STUDIES OF NIOBIUM CLUSTERS, S. M. E. GREEN, S. ALEX AND D. G. LEOPOLD, Department of Chemistry, University of Minnesota, Minneapolis MN 55455.

Negative ion photoelectron spectroscopy provides a means of obtaining vibrational data for atoms and small molecules "chemisorbed" on size-selected metal clusters. In the present study, Nb_3O^- , Nb_4O^- and Nb_4CO^- were prepared in a flowing afterglow ion-molecule reactor equipped with a metal cathode cluster source. The 488 nm photoelectron spectrum of the mass-selected Nb_3O^- anions shows a vertical transition to the ground state of neutral Nb_3O , with weak progressions in the Nb₃-O stretching ($710 \pm 20 \text{ cm}^{-1}$ in Nb_3O) and Nb₃ bending ($320 \pm 15 \text{ cm}^{-1}$ in both Nb_3O and Nb_3O^-) vibrational modes. These results indicate that the Nb_3O^- anion, like Nb_3O and Nb_3O^+ ,¹ has a planar C_{2v} structure with the O atom bridging two Nb atoms. The Nb_4O^- spectrum shows resolved transitions to the ground state of Nb_4O and to an excited electronic state lying $3050 \pm 20 \text{ cm}^{-1}$ higher in energy. In analogy with the Nb_3O results, the $670 \pm 20 \text{ cm}^{-1}$ frequency observed for the Nb_4O ground state is assigned to a metal-oxygen stretching mode, and the $215 \pm 15 \text{ cm}^{-1}$ and $195 \pm 15 \text{ cm}^{-1}$ frequencies observed in the ground and excited states, respectively, to a bending mode of the metal cluster. The electron affinities of Nb_3O and Nb_4O are 1.402 and 1.178 (± 0.006) eV, respectively. Preliminary, ongoing studies of mass selected Nb_4CO^- anions prepared under a variety of source conditions thus far suggest the presence of two isomers, one with a greatly weakened but intact CO bond as indicated by a very low CO stretching frequency of about 1300 cm^{-1} , and the other with the dissociated C and O atoms bound separately to the niobium cluster.

¹D.-S. Yang, M.Z. Zgierski, D.M. Rayner, P.A. Hackett, A. Martinez, D.R. Salahub, P.-N. Roy and T. Carrington, J. Chem. Phys. 103, 5335 (1995)

WH13

15 min 5:10

PRELIMINARY THEORETICAL AND EXPERIMENTAL STUDIES OF Al-GROUP14 DIATOMICS

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Two-color photoionization spectroscopy and density functional calculations have been used to investigate the Al-Group14 diatomics, AlSi, AlGe and AlSn. The bond lengths, vibrational frequencies, and dipole moments have been calculated using the DFT formalism for the lowest quartet and doublet of the neutrals, and the lowest singlet and triplet of the cations. The ground electronic state of the neutral is unequivocally the $^4\Sigma^-$ state arising from the $\pi^2\sigma^1$ configuration. Strong band systems lying in the 540-495 nm region have been observed using resonant two photon ionization (R2PI). At low resolution (0.1cm^{-1}), one band system appears to be $^4\Pi - ^4\Sigma$ in nature. Higher resolution spectra 0.005cm^{-1} should be available at the time of the meeting. Two-color photoionization efficiency spectroscopy yielded accurate ionization potentials. The electronic structure and bonding will be discussed at the meeting.

WH14

15 min 5:27

FOURIER TRANSFORM EMISSION SPECTROSCOPY OF THE $B^1\Pi - X^1\Sigma^+$, $C^1\Sigma^+ - X^1\Sigma^+$ AND $G^1\Pi - X^1\Sigma^+$ SYSTEMS OF ScH AND ScD

R. S. RAM AND P. F. BERNATH

The emission spectra of ScH and ScD have been observed in the 480 nm - $2.5\text{ }\mu\text{m}$ spectral region using a Fourier transform spectrometer. The molecules were excited in a scandium hollow cathode lamp operated with neon gas and a trace of hydrogen or deuterium. Three transitions with a common lower state, assigned as the ground $X^1\Sigma^+$ state, have been observed in the near infrared and visible regions. The ScH bands with 0-0 band origins at 5404, 13574 and 20547 cm^{-1} have been assigned as the $B^1\Pi - X^1\Sigma^+$, $C^1\Sigma^+ - X^1\Sigma^+$ and $G^1\Pi - X^1\Sigma^+$ transitions, respectively. A rotational analysis of the 0-0, 1-1, 1-0 and 2-1 bands of the $B^1\Pi - X^1\Sigma^+$ system, the 0-0 and 1-1 bands of the $C^1\Sigma^+ - X^1\Sigma^+$ system and the 0-0 band of the $G^1\Pi - X^1\Sigma^+$ system has been obtained. The principal molecular constants for the $X^1\Sigma^+$ state of ScH are: $\Delta G(1/2) = 1546.9730(14)\text{ cm}^{-1}$, $B_e = 5.425432(48)\text{ cm}^{-1}$, $\alpha_e = 0.124802(84)\text{ cm}^{-1}$ and $r_e = 1.775427(8)\text{ \AA}$.

The corresponding band systems of ScD have also been analyzed. A rotational analysis of the 0-0, 1-1 and 1-0 bands of the $B^1\Pi - X^1\Sigma^+$ system, the 0-0, 1-1, 0-1 and 1-2 bands of the $C^1\Sigma^+ - X^1\Sigma^+$ system and the 0-0 band of the $G^1\Pi - X^1\Sigma^+$ system has been obtained. The equilibrium molecular constants determined for the ground state of ScD are: $\omega_e = 1141.2650(31)\text{ cm}^{-1}$, $\omega_e x_e = 12.3799(15)\text{ cm}^{-1}$, $B_e = 2.787432(41)\text{ cm}^{-1}$, $\alpha_e = 0.045321(73)\text{ cm}^{-1}$ and $r_e = 1.771219(13)\text{ \AA}$.

The ScH assignments are supported by recent theoretical predictions made by Anglada et al. [Mol. Phys. 66, 541 (1989)] as well as the experimental results available for ScF and the isovalent YH and LaH molecules. Although some unassigned bands have been attributed to ScH and ScD by previous workers, there have been no previous analyses of ScH or ScD spectra.

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WH15

15 min 5:44

FOURIER TRANSFORM EMISSION SPECTROSCOPY OF THE $g^4\Delta - a^4\Delta$ SYSTEM OF FeF

R. S. RAM, P. F. BERNATH AND S. P. DAVIS

The emission spectrum of FeF has been observed in the near infrared region from 9000 cm^{-1} to 12000 cm^{-1} . The bands were excited in a high temperature carbon tube furnace and have been recorded using a Fourier transform spectrometer at a resolution of 0.02 cm^{-1} . The observed bands have been assigned as the 0-1, 0-0, 1-0, and 2-0 bands of the $g^4\Delta_i - a^4\Delta_i$ transition, analogous to the $F^4\Delta_i - X^4\Delta_i$ transition of FeH at $1\mu\text{m}$. Each vibrational band consists of four sub-bands assigned as $^4\Delta_{1/2} - ^4\Delta_{1/2}$, $^4\Delta_{3/2} - ^4\Delta_{3/2}$, $^4\Delta_{5/2} - ^4\Delta_{5/2}$ and $^4\Delta_{7/2} - ^4\Delta_{7/2}$. The rotational analysis of these bands has been performed and molecular constants have been determined. This work represents the first observation of the $g^4\Delta - a^4\Delta$ transition of FeF. We discuss the correspondence between the low-lying electronic states of FeF, FeH and Fe^+ .

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RA01

30 min 8:30

LASER FREQUENCY SPECTROSCOPY: A REVIEW, K. M. Evenson, Time and Frequency Division, National Institute of Standards and Technology, Boulder, Colorado, 80303

The extension of frequency measurements from the microwave to the ultra-violet has paved the way for the current revolution in ultra-high-resolution, high-accuracy spectroscopy. The extension of frequency measurements to the visible brought about the 1983 redefinition of the meter, fixing the value of the speed of light and making any frequency measured source a length standard. Lasers stabilized to sub-Doppler spectroscopic features have been found to be the most useful and accurate of these reference standards.

In the far-infrared (FIR) (from 10 to 200 wavenumbers) rotational transitions of CO, HF, and CH₃OH are three of the most commonly used standards. Far-infrared (FIR) spectrometers have been built using the difference frequencies from a pair of frequency-measured fluorescence-stabilized CO₂ lasers. This spectrometer provides frequency-based, tunable source of FIR radiation for measuring FIR spectra.

In the infrared, CO₂ and N₂O lasers stabilized to saturated fluorescence features in their respective lasing gases or to OsO₄ are excellent standards. We have built an ultra-high-resolution low-loss infrared laser oscillating on more than 400 lines of CO₂ or N₂O, provides a radiation source for the extension of frequency measurement to high J regular band lines and lines of other bands of CO₂ and N₂O. These measurements yield new molecular constants and a new set of standard frequencies and wavelengths in the infrared.

The CO laser oscillating in the 2000 wavenumber region is an excellent source for it can be stabilized on many other molecular transitions. Recently, it has been made to oscillate on the 0-1 band; thus, the laser can be stabilized on CO itself. This is one of the most stable new sources in this spectral region. The accidental coincidence of methane with the 3.39 micron He-Ne laser was one of the first highly stable lasers. It is now well measured and has served as an 88 Terahertz standard for many other measurements.

In the visible, a half a dozen iodine lines have been frequency measured and serve as wavelength and frequency standards in the visible. The best known of these is the iodine line used to lock the red helium-neon laser. The current "world record" frequency is that of the measurement of the Lyman alpha line of atomic hydrogen yielding a definitive value of the Rydberg constant.

The frequencies of many of these molecules is available in readily accessible locations, including the Internet. A summary of these will be presented.

RA02

15 min 9:05

Theory and Experimental Characterization of Lead Salt Diode Laser Frequency Modulation Spectroscopy

Khosrow Namjou, Chi Kong Ng, Edward A. Whittaker, *Department of Physics and Engineering Physics, Stevens Institute of Technology, Hoboken, NJ 07030.*

It has long been recognized that modulation techniques applied to tunable diode lasers improve sensitivity to the detection of weak molecular absorption lines. In this paper we will present the results of an extensive set of measurements designed to evaluate the efficacy of combining two levels of modulation, one at a relatively high frequency and usually termed frequency modulation spectroscopy and the second at a much lower frequency and usually termed wavelength modulation spectroscopy. The first modulation boosts the signal output of the photodetector to a sufficiently high frequency that laser technical noise has dropped below detector induced noise and thus allows maximum detection sensitivity. The second modulation adds the flexibility to adjust the modulation depth to discriminate against periodic interference fringes induced by windows in the laser beam path and which frequently limits the sensitivity boost afforded by the high frequency modulation.

In this paper we will present results of a complete modeling analysis of the dual modulation process as well as experimental measurements made on a tunable lead salt laser. We also discuss the applicability of these techniques to the new types of mid-infrared tunable diode lasers under development at various laboratories around the world.

RA03

15 min 9:22

High Precision Tunable Diode Laser Control: Application to the Study of Dicke Narrowing

A. Henry, D. Hurtmans, M. Margottin-Maclou and A. Valentin, *Laboratoire de Physique Moléculaire et Applications, C.N.R.S., Université Pierre et Marie Curie, Boîte 76, Tour 13, 4, Place Jussieu, F-75252 Paris Cedex 05, France.*

To stabilize the frequency, otherwise very unstable, of a T.D.L., its beam is sent through a Michelson interferometer controlled by a stabilized He-Ne laser. The T.D.L. is actively forced to maintain its emission at a wavelength value λ_d corresponding to an interference fringe of fixed order k_d . When D , the path difference of the interferometer, is changing, an optical device makes the vibration plane of the polarized He-Ne beam to rotate. When the azimuth plane is kept constant, D is also maintained constant, the fluctuation of k_d is reduced by nearly two orders of magnitude (*i.e.* 10^{-3} to 10^{-5} in the wavenumber units). Conversely, changing this azimuth by steps changes the value of D by increments ΔD . A change of λ_d is then induced in order to preserve the relation $D = k_d \lambda_d$. In addition, the usual intensity fluctuations are completely removed by a convenient double beam set-up. Finally, the signal-to-noise ratio obtained is better than 2000, allowing the measurement of gas traces.

Application:

At low pressure, the line profile narrowing resulting from the confinement of CO molecules by buffer gases (He, Ne, Ar, Xe and N₂) is studied to check the usual different collision models. The β^0 coefficient associated to this Dicke narrowing is compared to the dynamic friction coefficient β_{diff}^0 deduced from the diffusion constant, as a test for the validity of these different models.

When the pressure broadening becomes preponderant, the line profile must be determined carefully, taking into account the absorber speed dependent effect, in order to preserve the signification of the β^0 parameter—mainly when the perturber mass is greater than the active molecule one. A line asymmetry has been observed for the CO-Xe mixture, its magnitude being in agreement with the measured pressure shift.

RA04

15 min 9:39

SUB-DOPPLER SATURATION SPECTROSCOPY WITH THE COLOGNE THZ SPECTROMETER

S.P. BELOV, G. WINNEWISSER and TH. KLAUS, *I. Physikalisches Institut, Universität zu Köln, Zülpicher Str. 77, D-50937 Cologne, Germany.*

With the Cologne terahertz spectrometer (1) we have performed Lamb-dip measurements in the submillimeter wave region. The large output power of the frequency and phase stabilized backward wave oscillators (typically between 10 mW and 1 mW in the frequency range 300 GHz to 1000 GHz) was sufficient to saturate various molecular transitions. Together with the power reflected from the bolometer it has been possible to observe saturation dips in a free space absorption cell, whereby no further means have been required. Different molecules such as NH₃, HCl, and some of their isotopomers have been measured with sub-Doppler resolution at 570 GHz and 625 GHz. In the case of ammonia the ¹⁴N hyperfine structure of the lowest ro-inversion transitions $J = 1 \leftarrow 0$ in the ground and $J = 0 \leftarrow 1$ in the $v_2 = 1$ vibrational state has been fully resolved. The absolute frequencies have been measured with an accuracy of about 1 kHz. For the $v_2 = 1$ state the quadrupole coupling constant eqQ and the nuclear spin-rotation coupling constant C_N determined from this saturation dip measurements are $eqQ(v_2, J, K, s) = eqQ(1, 1, 0, s) = -4433.8(20)$ kHz and $C_N = 6.38(60)$ kHz.

The value of C_N for the vibrational ground state has been determined to be 6.7(3) kHz, whereby the eqQ value has been fixed to the number given by Hougen (2). This value is in very good agreement with the value $C_N = 6.80734$ kHz determined by Kukolich from two cavity maser measurements of the pure inversion transitions (3).

The present data confirm new possibilities for high resolution molecular spectroscopy in the submillimeter wave region. The parameters of the spectrometer and some recent results of sub-Doppler saturation measurements will be discussed.

(1) G. Winnewisser, *Vib. Spectrosc.* **8**, 241 (1995).

(2) J.T. Hougen, *J. Chem. Phys.* **57**, 4207 (1972).

(3) S.G. Kukolich, *Phys. Rev.* **156**, 83 (1967).

RA05

15 min 9:56

PRESSURE BROADENING AND SHIFT OF SOME NH₃ LINES MEASURED BY DIODE LASER SPECTROSCOPY

KOICHI M.T. YAMADA, M. FABIAN, *National Institute for Advanced Interdisciplinary Research, Tsukuba 305, Japan*; R. SCHIEDER, and G. WINNEWISSER, *I. Physikalisches Institut, Universität zu Köln, D-50937 Köln, Germany*.

Using the stabilized diode laser spectrometer in Cologne we have precisely determined pressure-induced line broadening and line shift coefficients of six rovibrational transitions in the ν_2 band of NH₃. Foreign gas effects due to O₂, N₂, H₂O, CO, He, and Ar have been investigated and the self-effects as well.

The high accuracy in the frequency position of the laser was achieved by stabilizing the diode laser on an interference maximum of a Fabry-Perot interferometer of variable optical length. The laser frequency was swept by tuning the cavity length of the étalon; the cavity length was monitored by a stabilized HeNe laser. A simultaneous recording of an NH₃ spectrum with a reference cell at a fixed pressure has been introduced for an absolute calibration. The line positions relative to reference lines have been measured to a precision of 300 kHz. A good signal-to-noise ratio was achieved by using a Herriott-type multi-reflection cell with a total path length of 46.86 m. This allowed to use very small NH₃ partial pressures of the order of a few hundred μ bar in the measurements of foreign gas effects to minimize the influence of NH₃ self-effects.

It turned out that contamination of the gas sample with H₂O imposed a serious problem upon the precise determination of the pressure effects, because of the large shift and broadening caused by H₂O. To remove any residual water contamination, the sample cell was connected to a cold finger submerged in a Dewar vessel filled with dry ice. The results of the present study are thus thought to be the most precise data of this kind now available.

RA06

15 min 10:13

THE VARIABLE TEMPERATURE PRESSURE BROADENING AND LINE SHIFT OF CO AND HDO IN COLLISION WITH HELIUM

M. M. BEAKY, T. M. GOYETTE, AND F. C. DE LUCIA

Pressure broadening and line shift cross sections for the $1 \leftarrow 0$ and $2 \leftarrow 1$ rotational transitions of carbon monoxide (CO) in collision with Helium (He) have been measured between 1 and 600 K. Measurements below 30 K were made using the collisional cooling technique, while measurements at higher temperatures were made in an equilibrium cell. The experimental apparatus and techniques employed in the study are described. The data are compared with theoretical predictions, and the significant differences between predictions based on the best available potential energy surface and the experimental results are discussed. Recent studies of the pressure broadening and line shifting of the $1_{10} \leftarrow 1_{11}$ rotational transition of deuterated water (HDO) in collision with He will also be presented.

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RA07**10 min 10:30****PRELIMINARY RESULTS FROM METHYL CHLORIDE COLLISIONAL COOLING EXPERIMENTS**

A. W. MANTZ, Department of Physics and Astronomy, Connecticut College, 270 Mohegan Ave., New London, CT 06320-4196; C. BALL, and F. DE LUCIA, Department of Physics, The Ohio State University, Columbus, Ohio 43210.

We made several modifications to a low temperature cell we described last year. The modifications were intended to make the cell more robust and to provide a cell with better vacuum integrity. The changes to the cell will be described briefly.

We will describe results obtained from measurements on the absorption bands of methyl chloride which are located in the seven micron spectral region.

Intermission**RA08****15 min 11:00**

High-Resolution $\nu_{\text{OH}} = 3 \leftarrow 0$ and $\nu_{\text{OH}} = 4 \leftarrow 0$ Overtone Spectroscopy of HOD, Joanna R. Fair, Ondrej Votava, and David J. Nesbitt

High-resolution (0.005 cm^{-1}) IR overtone excitation with an injection seeded optical parametric oscillator (OPO) is used to investigate the spectroscopy of HOD in the $\nu_{\text{OH}} = 3 \leftarrow 0$ region via room temperature photoacoustic detection methods. Comparison of the photoacoustic spectra from an $\text{H}_2\text{O}/\text{D}_2\text{O}/\text{HOD}$ mixture and from pure H_2O determines the lines corresponding to $\nu_{\text{OH}} = 3 \leftarrow 0$ absorptions in HOD. A prediction of the HOD spectrum in this region is generated from an extrapolation of $\nu_{\text{OH}} = 0$ and 1 rotational constants [W. S. Benedict, N. Gailar, and E. K. Plyler, J. Chem. Phys. **24**, 1139 (1956)] and from the $\nu_{\text{OH}} = 3 \leftarrow 0$ band origin calculated by Tennyson and coworkers [private communication]. This predicted spectrum enables the HOD $\nu_{\text{OH}} = 3 \leftarrow 0$ photoacoustic spectrum to be assigned; a fit of the experimental data produces the low-order rotational constants for this transition as well as a Birge-Sponer analysis of the overtone series. The vibrational dependence of the HOD rotational constants is demonstrated to be quite linear in ν_{OH} , permitting reliable extrapolation to the $\nu_{\text{OH}} = 4$ manifold. As a result, the $\nu_{\text{OH}} = 0, 1$ and 3 constants can be used to predict the spectrum of HOD $\nu_{\text{OH}} = 4 \leftarrow 0$, which now enables the assignment of the vibrationally mediated photodissociation spectrum measured by Crim and coworkers [R. B. Metz, J. D. Thoemke, J. M. Pfeiffer, and F. F. Crim, J. Phys. Chem. **99**, 1744 (1993)]. The overtone spectroscopic data for HOD is further confirmed in double resonance IR and UV photolysis of HOD and HOD-containing clusters in slit supersonic expansions.

Joanna R. Fair: JILA, National Institute of Standards and Technology and Department of Chemistry and Biochemistry, University of Colorado, Boulder, Colorado 80309-0440.

RA09

10 min 11:17

LASER SPECTROSCOPY OF 3V, 5V and 6V VIBRATION - ROTATION BANDS OF HBr

N. NISHIMIYA, T. YUKIYA AND M. SUZUKI, *Dept. of Electronic Engineering, Tokyo Institute of Polytechnics, Iiyama 1583, Atsugi City, 243-02 Kanagawa, Japan.*

The vibration - rotation spectrum of $\text{H}^{79/81}\text{Br}$ have been studied using a GaAs semiconductor laser and a titanium sapphire ring laser in the near infrared region. The rotational fine structures up to $J=15$ could be detected using a 20 m absorption cell. About 100 lines have been assigned in $v = 3 \leftarrow 0$, $5 \leftarrow 0$ and $6 \leftarrow 0$ bands with a resolving power of 0.001 cm^{-1} . Spectroscopic constants have been calculated with a least-squares fitting procedure by using the spectroscopic constants of $v = 0$ reported by Lonardo and Fusina (1). The values in cm^{-1} are determined as below;

$G_3 - G_0 = 7405.2618(8)$	$B_3 = 7.656220(15)$	$D_3 \times 10^4 = 3.3701(5)$
$7404.1937(10)$	$7.653951(18)$	$3.3673(5)$
$G_5 - G_0 = 11887.9321(5)$	$B_5 = 7.190004(18)$	$D_5 \times 10^4 = 3.3661(10)$
$11886.2940(5)$	$7.187967(18)$	$3.3640(10)$
$G_6 - G_0 = 13990.8191(10)$	$B_6 = 6.953022(45)$	$D_6 \times 10^4 = 3.3777(35)$
$13988.9406(3)$	$6.951116(15)$	$3.3782(13)$

The numbers given in the upper rows are those of I^{79}Br . The Dunham's coefficients of HBr have also been determined by a joint analysis with the constants reported by the references (1, 2).

(1) G. Di Lonardo, and L. Fusina, *J. Mol. Spectrosc.*, **148**, 86-92 (1991).

(2) V. Braun, and P. F. Bernath, *J. Mol. Spectrosc.*, **167**, 282-287 (1994).

RA10

15 min 11:29

VIBRATIONAL-ROTATIONAL-TUNNELING SPECTROSCOPY OF $\text{N}_2\text{-D}_2\text{O}$ WITH AN ALL SOLID STATE, OPTICAL HETERODYNE, SUBMILLIMETER-WAVE SPECTROMETER

PIN CHEN, *Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, CA 91125*; GEOFFREY A. BLAKE, *Division of Geological and Planetary Sciences, California Institute of Technology, Pasadena, CA 91125*.

Recent advances in the fabrication of ultrafast low-temperature-grown GaAs optoelectronic devices have made possible the generation of spectroscopically significant amounts of tunable, cw far-IR radiation via optical heterodyne processes. We will present VRT spectra of the $\text{N}_2\text{-D}_2\text{O}$ complex using an all-solid-state, passively frequency-stabilized, optical-heterodyne FIR spectrometer.

RA11**15 min 11:46**

LASER SIDE BAND SPECTRUM OF THE ν_2/ν_4 DIAD OF AsH₃ AND PH₃,
SATURATION OF PERTURBATION ALLOWED TRANSITIONS, G. Spiegl,
A. Ainetshian, and W.A. Kreiner, Department of Chemistry, University of Ulm, D-89069
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The ν_2/ν_4 ($907/999\text{ cm}^{-1}$) diad of the arsine molecule has been investigated between
 875 cm^{-1} and 1086 cm^{-1} with tunable IR laser sidebands at an absolute accuracy of $<150\text{ kHz}$
and a resolution of better than 300 kHz . Eleven A_1/A_2 doublets have been resolved for the
first time. Three perturbation allowed transitions could be saturated. A fit of 70 parameters
achieved a standard deviation of 156 kHz .

On the phosphine molecule, which exhibits a fairly weak absorption spectrum on the ν_2/ν_4
($992/1118\text{ cm}^{-1}$) diad, 48 allowed saturated transitions could be observed, among them four
 $K=6$ doublets. Including data from the literature an overall standard deviation of 1.2 Mhz was
obtained.

RA12**15 min 12:03**FAR-INFRARED LASER STARK SPECTROSCOPY OF PH₃

M. Jackson, G. R. Sudhakaran, and E. Gansen

The Stark spectrum of PH₃ has been investigated in the far-infrared region using the DCN
laser. Several families of absorption lines were observed in both parallel and perpendicular
polarizations using electric fields up to $57\,000\text{ V/cm}$. The multiplet transitions, independently
observed with two different DCN laser lines, were assigned as $J_K = 6_K \leftarrow 5_K$ E, $K = 1, 2, 4$,
and 5 along with $J_K = 6_3 \leftarrow 5_3$ $A_{1,2} \leftarrow A_{2,1}$ in the $\nu_2 = 1$ vibrational state. In addition, several
absorption lines belonging to the forbidden zero-field transitions $J_K = 6_3 \leftarrow 5_3$ $A_{1,2} \leftarrow A_{1,2}$ have
been observed for the first time. Accurate zero-field frequencies for all assigned transitions will
be presented.

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RB01

15 min 8:30

REMPI SPECTRA AND *AB INITIO* CALCULATIONS OF BENZOTRIAZOLE AND ITS WATER CLUSTERS

MICHAEL SCHMITT, WOLFGANG ROTH, CHRISTOPH JACOBY, KARL KLEINERMANN

Institut für Physikalische Chemie und Elektrochemie I

Heinrich-Heine Universität Düsseldorf, 40225 Düsseldorf, Germany

The 1+1 resonance ionization (REMPI) spectra of benzotriazole (BT) and its hydrogen bonded water clusters benzotriazole(H_2O)_n, $n=1-3$ have been measured in a molecular beam between 34919 cm^{-1} and 36100 cm^{-1} . The electronic origin of the monomer can only be determined by 1+1 two color REMPI, as the difference between S_1 - and ionization energy is slightly larger than the $S_0 - S_1$ energy difference. Due to the low ionization excess energy, fragmentation of the clusters is small. Certainty about the existence of more than one conformer (for both monomer and clusters) in the molecular beam can only be obtained by spectral hole burning.

Stability and vibrational frequencies of the two possible tautomers (1H and 2H) of BT are calculated by *ab initio* and density functional calculations. Many possible structures had to be calculated because both water and BT can act as proton donor and acceptor. Cyclic structures for BT(H_2O)₁ were found to be nearly as stable as a trans-linear arrangement of the hydrogen bond. The transition state structure, which is a saddle point at the potential surface, is calculated for the BT(H_2O)_n clusters and a mechanism for the H-bond subsidized tautomerisation is proposed. For a complete assignment of the cluster spectra, low frequency intermolecular vibrations and torsional motion of the water molecule have to be discussed.

RB02

15 min 8:47

FLUORESCENCE DIP INFRARED SPECTROSCOPY (FDIRS) OF JET-COOLED 5-HYDROXYTROPOLONE

R. K. FROST AND T. S. ZWIER, *Department of Chemistry, Purdue University, West Lafayette, IN 47907-1393.*

Ground state infrared spectra of jet-cooled 5-hydroxytropolone are recorded in the region from 2600 to 4200 cm^{-1} . In this technique, a near-ultraviolet laser pulse (not tuned) excites a chosen fluorescence transition in order to monitor a unique ground state population in the molecular beam. A high-power infrared pulse generated from a Nd:YAG-pumped OPO system is tuned through the infrared region. The infrared is spatially overlapped with the near-ultraviolet but precedes it by roughly 100 ns. When resonance with an infrared transition occurs, population is excited out of the ground state which is manifested as a dip in fluorescence signal. Ground state infrared spectra of both the syn and anti conformations of 5-hydroxytropolone are recorded with excellent signal-to-noise. Large red shifts are observed for the intramolecularly hydrogen bonded O-H stretch in 5-hydroxytropolone which contrast to characteristic shifts for intermolecularly hydrogen bonded modes. Additionally, the syn and anti conformations show distinct infrared spectra which will be discussed in light of the density of bath states and the interaction between the asymmetric syn and anti potential energy wells.

RB03

15 min 9:04

INFRARED SPECTROSCOPY OF JET-COOLED TROPOLONE AND TROPOLONE-OD IN THE O-H AND C-H STRETCH REGION

C. A. ARRINGTON, R. K. FROST, F. C. HAGEMASTER, AND T. S. ZWIER, *Department of Chemistry, Purdue University, West Lafayette, IN 47907-1393.*

Fluorescence-dip infrared spectroscopy has been employed to record the vibrational spectra of gas phase tropolone and tropolone-OD in the O-H and C-H stretch region for the first time. Tropolone, an pseudo-aromatic ringed system, possesses a symmetric $O-H-O$ tunneling coordinate which produces a ground state tunneling splitting of 0.99 cm^{-1} . Use of a two laser depletion scheme allows separate infrared spectra to be recorded for both the lower (a_1 symmetry) and upper (b_2 symmetry) ground state tunneling levels. In each spectrum, a single transition ascribable to the O-H stretch is observed. The (a_1) O-H stretch at 3134.9 cm^{-1} is close in energy to the (b_2) O-H stretch observed at 3133.9 cm^{-1} indicating that the transitions are to the same excited state tunneling level. Tropolone-OD was investigated in order to identify the C-H stretch vibrations which are close in energy to the red-shifted O-H stretch of tropolone. The spectroscopic results along with recent *ab initio* calculations are discussed in terms of the hydrogen tunneling motion in tropolone.

RB04

15 min 9:21

FLUORESCENCE-DIP INFRARED SPECTROSCOPY OF THE TROPOLONE-H₂O COMPLEX

F. C. HAGEMASTER, C. A. ARRINGTON, R. K. FROST, D. SCHLEPPENBACH, AND T. S. ZWIER, *Department of Chemistry, Purdue University, West Lafayette, IN 47907-1393*; K. D. JORDAN, *Department of Chemistry, University of Pittsburgh, Pittsburgh, PA 15260.*

Fluorescence-dip infrared spectroscopy (FDIRS) is used to probe the effect of solvent binding by water on the intramolecular H-atom tunneling in tropolone. As with the bare molecule in the adjoining presentation, the FDIR spectrum of the jet-cooled tropolone-H₂O complex is recorded in the O-H and C-H regions. The spectrum possesses distinct absorptions due to the water free OH, water hydrogen-bonded OH, and tropolone OH. Extensive *ab initio* calculations on tropolone-H₂O are carried out at both the MP2 and Becke3LYP levels of theory. Two isomers for the complex are identified with binding energies and vibrational frequencies quite similar to one another. The experimental evidence does not conclusively distinguish between these two possibilities, though discussion will focus one that is more in keeping with the data as a whole.

RB05

15 min 9:38

Time Resolved Stimulated Emission Pumping Of Bianthryl-Water Complexes

BRIAN A. PRYOR, PETER M. ANDREWS, and MICHAEL R. TOPP, *Department of Chemistry, University of Pennsylvania, Philadelphia, Pennsylvania 19104.*

Bianthryl-water complexes in a supersonic jet have been investigated using a variety of spectroscopic techniques. The laser induced fluorescence spectrum of this complex displays a red shift of a torsional progression similar to that of bare bianthryl. The hole-burning spectra show this progression results from a single species. Solution phase studies of bianthryl in polar solvents show a pronounced red shift in emission which has been attributed to charge transfer. The dispersed fluorescence spectra of the bianthryl complex with a single water molecule show a non-resonant, structureless, emission also which is evidence of charge transfer character. This structureless emission suggests a very fast barrier crossing, therefore a picosecond transient approach is necessary. Time resolved stimulated emission pumping was done on this complex to resolve the resonant fluorescence spectrum. The data are then used to investigate the combination of a single excitation and multiple emission excited-state torsional potential energy surfaces.

RB06**15 min 9:55****Double Resonance Study of Hydrogen-Bonded Perylene Complexes**

PETER M. ANDREWS, BRIAN A. PRYOR, MICHAEL R. TOPP, Department of Chemistry, University of Pennsylvania, Philadelphia, PA 19104 andrews@a.chem.upenn.edu.

Spectral hole-burning has been performed on different aggregate levels of the hydrogen-bonding species perylene/water, perylene/methanol, etc.. This and other spectroscopic techniques are used in order to examine how a hydrophobic molecule such as perylene affects the formation of hydrogen-bonded clusters through the study of low-frequency modes and cluster dynamics. Several features have been resolved showing red shifted excitation frequencies relative to the bare parent molecule, as well as slightly blue shifted frequencies, as for example, in the case of the water complex. Low frequency mode structure is superimposed on the strong vibronic resonances of the complex, suggesting the possibility of a tumbling motion on the perylene plane. In order to elucidate the structure of some of the less facile species, rotational coherence spectroscopy is performed, resulting in the proposal of several possible structures. Picosecond time-resolved fluorescence spectroscopy, as well as dispersed fluorescence spectroscopy, is also performed in order to characterize the presence of any excited state relaxation pathways at the zero point and higher vibronic levels.

Intermission**RB07****10 min 10:30**

VIBRATIONAL OVERTONE SPECTROSCOPY OF ORGANOMETALLIC COMPLEXES, A. V. FEDOROV, D. SNAVELY
Center for Photochemical Sciences, Department of Chemistry, Bowling Green State University, Bowling Green, OH, 43403.

The spectra of chromocene, manganocene and cyclopentadienyl manganese tricarbonyl have been recorded at the third overtone region ($\Delta v=4$) using intracavity photoacoustic spectroscopy. The interpretation of these spectra and their correlation with the electronic structure of the complexes will be presented. These investigations will help in the understanding of metal bonding to a conjugated π -systems and explain the catalytic reactivity of organometallic complexes.

This work is an expansion of previous investigations involving ferrocene and related compounds (acetylferrocene, ruthenocene, cyclopentadienyl titanium tetrachloride). Three additional blue-shifted transitions which were absent in the spectrum of the pure hydrocarbon ligand (cyclopentadiene) have been observed for those complexes.¹ These absorptions were assigned to the different combinations of the C-H stretch with C-C stretches and C-H bends of the cyclopentadienyl ring.

Cyclopentadienyl manganese tricarbonyl possesses a spectrum similar to ferrocene and related compounds. Spectra of chromocene and manganocene are different from those of ferrocene and others. We explain these differences in terms of the different electronic structures of the complexes.

1. T. Van Marter, C. Olsen, D.L. Snavely, *J. Phys. Chem.* **98**, 5404(1994).

RB08

15 min 10:42

STRUCTURE AND DYNAMICS OF ANILINE-AR FROM HIGH RESOLUTION ELECTRONIC SPECTROSCOPY IN THE GAS PHASE, * WAYNE E. SINCLAIR AND DAVID W. PRATT

We report studies of the rotationally resolved $S_1 \leftarrow S_0$ electronic spectra of aniline and its van der Waals complex with a single Ar atom. Analysis of these spectra leads to a determination of the vibrationally averaged structures of the bare molecule and the complex in the two electronic states. Aniline itself is pyramidally distorted at the NH_2 group in the S_0 state. Attachment of the Ar atom on the side of the ring opposite to the two NH bonds converts the symmetric double well along the inversion coordinate to an asymmetric one, in the ground state. The excited state is quasi-planar along this coordinate. At higher vibrational energies in the S_1 state, we also observe in the spectra of the complex line broadenings and spectral perturbations, a consequence of vibrational predissociation (VP). The important role of intra-intermolecular mode mixing (i.e., IVR) in promoting the VP process is elucidated from these data.

*Work supported by NSF (CHE-9224398)

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RB09

15 min 10:59

STRUCTURES AND VIBRATIONS OF PHENOL- NH_3 AND PHENOL- $(NH_3)_2$ -CLUSTERS

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The phenol-ammonia complexes have been investigated experimentally by two colour 1+1 resonance ionization (REMPI) and mass resolved hole burning spectroscopy and theoretically by *ab initio* methods at the HF/6-31G(d,p) and HF/6-31++G(d,p) level of theory. With these theoretical methods the structures and vibrational frequencies of the clusters could be determined. By means of spectral hole burning, four bands in the low frequency region could be assigned to specific intermolecular vibrations of the 1:1 complex. Transitions arising from the threefold rotation of the NH_3 moiety could be correlated with calculated frequencies for this motion. Barriers of 43 cm^{-1} for the S_0 and 53 cm^{-1} for the S_1 state were obtained.

Other strong bands in the one-color REMPI spectrum of the 1:1 cluster could be assigned to phenol- $(NH_3)_2$ by two-color experiments. The lowest frequency transition at 35545 cm^{-1} is tentatively assigned to the pure electronic $S_1 \leftarrow S_0$ transition. A progression of approximately 20 cm^{-1} is built upon this electronic origin, as well as on a transition at 265 cm^{-1} . Every line within both progressions splits by about 2 cm^{-1} . Hole burning spectroscopy shows that the splitted lines stem from different conformers of the cluster. For the calculated cyclic geometry of the cluster there are two possible conformers with the H-atom of the $N \cdots H \cdots N$ hydrogen bond lying above or below the ONN plane. The significance of cyclic structures in regard to intracluster proton transfer is discussed.

RB10

15 min 11:16

THE $T_1(n\pi^*) \leftarrow S_0$ LASER INDUCED PHOSPHORESCENCE EXCITATION SPECTRUM OF ACETALDEHYDE IN A SUPERSONIC FREE JET: TORSION AND WAGGING POTENTIALS IN THE LOWEST TRIPLET STATE, H. LIU AND E. C. LIM, Department of Chemistry, The University of Akron, Akron, OH 44325-3601; C. MUNOZ-CARO AND A. NINO, E.U. Informática, Universidad de Castilla-La Mancha, Ronda de Calatrava 5, 13071 Ciudad Real, Spain; R. H. JUDGE, Department of Chemistry, University of Wisconsin-Parkside, Kenosha, WI 53141-2000; D. C. MOULE, Department of Chemistry, Brock University, St. Catharines, Ontario, L2S 3A1, Canada.

The laser induced $T_1(n\pi^*) \leftarrow S_0$ phosphorescence excitation spectrum of jet-cooled acetaldehyde has been observed for the first time with a rotating slit nozzle excitation system. The vibronic origins were fitted to a set of levels that were obtained from a Hamiltonian that employed flexible torsion-wagging large amplitude coordinates. The potential surface extracted from the fitting procedure yielded barriers to torsion and inversion of 614.30 and 864.45 cm^{-1} , respectively. Minima in the potential hypersurface at $\theta = 60.30^\circ$ and $\alpha = 42.16^\circ$ defined the equilibrium positions for the torsion and wagging coordinates. A comparison to the corresponding S_1 -state parameters showed that the torsion barrier (in cm^{-1}) does not greatly change, $S_1/T_1 = 710.8/614.3$, whereas the barrier height for the wagging-inversion barrier increases dramatically, 574.4/864.5.

RB11

15 min 11:33

ELECTRONIC SPECTROSCOPY OF DIPHENYLAMINE AND ITS SOLVENT CLUSTERS

IGOR V. TRETIKOV, JOHN R. CABLE, *Department of Chemistry and Center for Photochemical Sciences, Bowling Green State University, Bowling Green, OH 43403; , .*

The vibrationally resolved electronic spectra of diphenylamine and several isotopically substituted derivatives were recorded using two-photon ionization under supersonic jet expansion conditions. Spectral evidence is consistent with the equivalence of the two phenyl rings which suggests a C_2 symmetry ground state in which the central nitrogen atom is in a planar configuration. Analysis of the spectrum of diphenylamine clustered with water shows that the solvent has a large influence on the chromophore structure. This contrasts with the observations obtained for diphenylamine clustered with inert gases and nitrogen.

RB12

15 min 11:50

Ab initio study of the np (n=3-5) and 4s-3d Rydberg complexes of acetylene.

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Large scale internally-contracted MRCI calculations have been performed on the singlet states arising from the np (n=3-5) and 4s-3d Rydberg complexes of acetylene. Term energies are predicted with an accuracy of about 0.05 eV, leading to a reliable energy scale helpful for the interpretation of MPI spectra^a. The Rydberg-valence and 4s-3d mixings are quantified from the analysis of the wave functions, and the corresponding anisotropy of the ionic core along the Rydberg series is discussed. Quantum defect values are reported. The calculations also investigate the region of the potential energy surfaces where the whole np series is crossed by doubly excited singlet valence states, namely by the $C' \ ^1A_g$ state^b. This region corresponds to intermediate geometries between those of the linear ground state and of the trans bent C' state, i.e. around $R_{CC} = 1.4 \text{ \AA}$ and $HCC = 140^\circ$. The predissociative features of both the C' and the np Rydberg states are explained from the high degree of Rydberg valence mixing in this region.

^aJ.H. Fillion, A. Campos, J. Pedersen, N. Shafizadeh and D. Gauyacq, to be published.

^bJ. Liévin, J. Mol. Spectrosc. **156**, 123 (1992).

RC01

15 min 8:30

Optical Stark Spectroscopy of CaCH_3

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An intense pulsed supersonic molecular beam sample of CaCH_3 was produced using a laser ablation/reaction source. The high resolution (50 MHz FWHM) laser induced fluorescence spectrum of the ($K'=1-K''=0$) $\tilde{A}^2\text{E}-\tilde{X}^2\text{A}_1$ band system (origin = 14743 cm^{-1}) was recorded and fitted to produce an improved set of spectroscopic parameters. The resultant parameters were in agreement with those obtained in a previous Doppler limited study^a. A number of the transitions involving the lowest J levels were also recorded in the presence of variable static electric field. The Stark shifts and splittings were fitted to obtain dipole moments of 2.62(3) D and 1.69(1) D for the $\tilde{X}^2\text{A}_1$ and $\tilde{A}^2\text{E}$ states, respectively. The dipole moments were predicted using an electrostatic polarizability model^{b,c} that had successfully predicted the dipole moments of CaCCH ^d. The predicted values, 1.78 D $\tilde{X}^2\text{A}_1$ and 1.20 D $\tilde{A}^2\text{E}$, are in reasonable agreement with experiment.

^aC. R. Brazier and P. F. Bernath, *J. Chem. Phys.* **91**, 4548 (1989).

^bT. Törring, W. E. Ernst and J. Klönder, *J. Chem. Phys.* **90**, 4927 (1989).

^cJ. M. Mestdagh and J.-P. Visticot, *Chem. Phys.* **155**, 19 (1991).

^dA. J. Marr, J. Perry and T. C. Steimle, *J. Chem. Phys.* **103**, 3861 (1995).

RC02

10 min 8:47

High Resolution Laser Spectroscopy of the $\tilde{C}^2\text{A}_1-\tilde{X}^2\text{A}_1$ Transition of CaNH_2

Zulfikar Morbi, Chunfeng Zhao, P.F. Bernath, *Center for Molecular Beams and Laser Chemistry, University of Waterloo, Waterloo, Ont., Canada, N2L 3G1.*

The high resolution excitation laser spectrum of the $\tilde{C}^2\text{A}_1-\tilde{X}^2\text{A}_1$ transition of CaNH_2 was recorded with a laser ablation/supersonic molecular beam source. The molecule was made by ablating Ca metal with the second harmonic of a pulsed Nd:YAG laser followed by reaction of with 5% NH_3 seeded in Ar(or He). Laser induced fluorescence spectra was recorded 12 cm downstream from the nozzle with a single-mode cw ring dye laser. Molecular constants for the $K'_a=0-K''_a=0$ sub-band have been determined. The $K'_a=1-K''_a=1$ sub-band is currently being analysed.

RC03

10 min 8:59

High Resolution Laser Spectroscopy of the $\tilde{C}^2\text{A}_1-\tilde{X}^2\text{A}_1$ Transition of SrNH_2 and $\tilde{B}^2\text{B}_1-\tilde{X}^2\text{A}_1$ Transition of CaNH_2

Chunfeng Zhao, J.W. Hepburn, P.F. Bernath, *Center for Molecular Beams and Laser Chemistry, University of Waterloo, Waterloo, Ont. Canada, N2L 3G1.*

The high-resolution laser excitation spectrum of $\tilde{C}^2\text{A}_1-\tilde{X}^2\text{A}_1$ transition of SrNH_2 and $\tilde{B}^2\text{B}_1-\tilde{X}^2\text{A}_1$ transition of CaNH_2 were recorded. The SrNH_2 and CaNH_2 molecules were made by pulsed laser ablation of Sr and Ca metal rods followed by reaction with NH_3 . A cw dye laser was used to detect the laser induced fluorescence from a supersonic beam. The measured line positions have been fitted to give molecular constants for the electronic states.

RC04

15 min 9:11

LASER SPECTROSCOPY OF CCH IN THE 36600–39700 cm^{-1} REGION, WHE-YI CHIANG AND YEN-CHU HSU Institute of Atomic and Molecular Sciences, Academia Sinica, P. O. Box 23–166, Taipei 107, Taiwan, Republic of China and Department of Chemistry, National Taiwan University, Taipei 107, Republic of China.

In the 36600–39700 cm^{-1} range, eight new bands of CCH $\tilde{B}^2A' \leftarrow \tilde{X}^2\Sigma^+$ transition were observed by laser-induced fluorescence. By rotational analysis, they have been assigned as transitions from low vibronic levels, $\tilde{X}(0, v_2, v_3)$ ($v_2=2-4$ and $v_3=0-1$) of CCH to two vibrational levels (T, T+1221) of the \tilde{B} state. Most of these bands were difficult to be detected if a acetylene/argon or helium gas mixture was photolyzed to produce CCH. Due to population transfer, via collisions with SF_6 , from higher vibronic levels of CCH which were predominantly produced in the 193.3 nm photolysis of acetylene, spectral intensities of these bands were thus enhanced. Spectroscopic parameters of $\tilde{X}(0, 2^0, 0)$, $\tilde{X}(0, 2^2, 0)$, $\tilde{X}(0, 2^2, 1)$, and $\tilde{B}(T+1221)$ were obtained for the first time. Spectral lines of transition $\tilde{B}(T) \leftarrow \tilde{X}(0, 3^{b3}, 0)$ recorded in a supersonic beam were also included in a simultaneous fit, spectroscopic parameters of $\tilde{X}(0, 3^{b3}, 0)$ were accordingly better determined in this work than our previous reports.^{a,b}

The vibronic energy levels $\tilde{X}(0, v_2^l, v_3)$ ($v_3=0-2$) of CCH up to 5500 cm^{-1} were approximated as three anharmonic oscillators, where ν_2 is 401 cm^{-1} . The anharmonicities and g_{11} 's obtained from the fit will be given.

^aY.-C. Hsu, J. J.-M. Lin, D. Papoušek, and J.-J. Tsai, J. Chem. Phys. 98, 6690(1993).

^bY.-C. Hsu, Y.-J. Shiu, and C.-M. Lin, J. Chem. Phys. 103, 5919(1995).

RC05

15 min 9:28

FLUORESCENCE LIFETIMES OF THE \tilde{B}^2A' STATE OF CCH, WHE-YI CHIANG AND YEN-CHU HSU Institute of Atomic and Molecular Sciences, Academia Sinica, P. O. Box 23–166, Taipei 107, Taiwan, Republic of China and Department of Chemistry, National Taiwan University, Taipei 107, Taiwan, R. O. C.

Three vibrational levels of the \tilde{B}^2A' state of CCH have been observed by laser-induced fluorescence. They were assigned as T, T+775, and T+1221 where level T was first identified as a vibrational level of the \tilde{B} state.^a J, K-resolved fluorescence lifetimes of these vibrational levels of the \tilde{B} state have been determined in a supersonic molecular beam. It was found that the lifetimes of levels T+775 and T+1221 were significantly shorter than that of level T. Lifetimes of various ro-vibrational levels will be presented. The previously reported CC-H bond energies range from 95.6 to 116.3 kcal/mol,^b resulting difficulty in assigning the onset of the dissociation process, $\text{CCH}(\tilde{X}^2\Sigma^+) \rightarrow \text{C}_2(\tilde{X}^1\Sigma_g^+) + \text{H}(\tilde{2}S_{1/2})$. We speculated that lifetimes quenched at levels T+775 and T+1221 were due to predissociation. Comparison of $D_0^0(\text{CC-H})$ estimated from this work and other literature values will be given.

^aYen-Chu Hsu, Ying-Jen Shiu, and Chi-Min Lin, J. Chem. Phys. 103, 5919(1995).

^bD. Dufloot and J.-M. Robbe, and J.-P. Flament, J. Chem. Phys. 100, 1236(1994).

RC06**15 min 9:45**

PULSED DISCHARGE JET SPECTROSCOPY OF THE $\tilde{A}^1A' - \tilde{X}^1A'$ BAND SYSTEMS OF SILYLENES AND GERMYLENES, WARREN W. HARPER, H. HARJANTO, AND DENNIS J. CLOUTHIER, Department of Chemistry, University of Kentucky, Lexington, KY 40506-0055.

Jet-cooled laser induced fluorescence spectra of HSiCl, DSiCl, HSiBr, DSiBr, HGeCl, and DGeCl have been obtained by diluting appropriate trihalosilane or germane precursors with argon and expanding them through a pulsed electric discharge. The upper state harmonic frequencies, anharmonicities, and isotope shifts were obtained from detailed vibrational analyses of the spectra. In favorable cases, the 0_0^0 bands were recorded at 0.05 cm^{-1} resolution and rotationally analyzed, providing ground and excited state rotational constants. The vibrational and rotational data have been used to obtain ground and excited state structures and upper state harmonic force fields for these reactive intermediates.

Intermission**RC07****15 min 10:20**

REMPI SPECTROSCOPY OF THE $3p\pi^2\Pi$ RYDBERG STATE OF HCO

Hartmut G. Hedderich, Eric E. Mayer, and Edward R. Grant, *Department of Chemistry, Purdue University, West Lafayette, IN 47907-1393.*

The (010), (020), (030), and (001) bands of the $3p\pi^2\Pi$ Rydberg state of the formyl radical have been observed by resonant (1+1) photon ionization spectroscopy from the $^2A'$ vibronic ground state. Subbands have been re-assigned considering the $D_{\infty h}$ symmetry of HCO in the $3p\pi$ -state. Renner-Teller effect and Fermi resonances have been analyzed for different subbands.

RC08**15 min 10:37**

THE VIBRATIONAL/ROTATIONAL ASSIGNMENT OF THE LIF SPECTRUM OF THE $\tilde{A}^2A_1 - \tilde{X}^2E$ ELECTRONIC TRANSITION OF THE METHOXY RADICAL

MICHAEL B. PUSHKARSKY, DAVID E. POWERS, and TERRY A. MILLER, *The Ohio State University, Department of Chemistry, The Laser Spectroscopy Facility, 120 West 18th Ave., Columbus, OH 43210.*

The methoxy radical was revisited and its LIF spectrum in a free jet expansion was recorded using a specially designed extension attached to the nozzle. This modification allowed us to cool molecules vibrationally and observe only transitions from the vibrationless level of the ground electronic state. This gave rise to a dramatic simplification of the spectrum, compared to previous observations.

However, even a vibrationally cold spectrum is quite complex because the methoxy radical ground state has E symmetry and thus exhibits Jahn-Teller distortion giving rise to transitions from the vibrationless level of the lower electronic state to both symmetric and asymmetric vibronic levels of the upper electronic state.

We have used the rotational analysis of the spectra to distinguish between bands in the LIF spectrum due to transitions to symmetric and asymmetric modes.

RC09

15 min 10:54

FLUORESCENCE DEPLETION SPECTROSCOPY FOR MAPPING DARK VIBRONIC LEVELS IN THE \tilde{A}^2A_1 STATE OF THE METHOXY RADICAL

DAVID E. POWERS, MICHAEL B. PUSHKARSKY, and TERRY A. MILLER, *The Ohio State University, Department of Chemistry, The Laser Spectroscopy Facility, 120 West 18th Ave., Columbus, OH 43210.*

Fluorescence Depletion Spectroscopy (FDS) has been used to obtain information on vibronic levels in the \tilde{A}^2A_1 state of the methoxy radical. This technique has proven to be very powerful for obtaining a variety of different types of information. We have used FDS to map, at rotational resolution, the dark predissociative vibronic levels of methoxy which start around 6 quanta of the C-O stretching mode (about 3800 cm^{-1} above the origin). The photofragmentation is fairly mode selective requiring significant energy in the C-O stretch before predissociation can occur. The dark states have been observed to $\approx 5400\text{ cm}^{-1}$ above the $\tilde{A}-\tilde{X}$ electronic origin.

The FDS technique has also been used to distinguish between bands in the LIF spectra that are hot bands and features originating from the vibrationless level of ground state. In addition, the rotational selectivity of the technique has been used to facilitate the assignment of the rotational structure for some of the vibronic transitions observed in the LIF spectrum. By scanning the dump laser over a band that has been previously rotationally assigned, the rotational quantum numbers of the LIF transition being probed can be determined. If similar spectra are obtained by probing each of the populated ground state rotational levels the task of rotational assignment can be greatly simplified.

RC10

15 min 11:11

ROTATIONAL ANALYSIS OF A-E AND E-E VIBRONIC BANDS OF CF_3S

MIN-CHIEH YANG, DAVID E. POWERS, CHRISTOPHER C. CARTER, JAMES M. WILLIAMSON, and TERRY A. MILLER, *The Ohio State University, Department of Chemistry, The Laser Spectroscopy Facility, 120 West 18th Ave., Columbus, OH 43210.*

Rotationally resolved spectra of jet-cooled CF_3S have been obtained. The rotational analysis of the origin band shows that it is an a-e type vibronic transition. This is also consistent with the $\tilde{A}^2A_1 - \tilde{X}^2E$ electronic transition, expected for molecules of this type. This indicates that CF_3S has nominal C_{3v} symmetry in both its ground and first excited electronic state.

In addition to the origin band, several transitions to excited vibrational levels of the \tilde{A} state have been observed. Some of these transitions are vibronically a-e while others appear to be e-e, presumably induced by Jahn-Teller interaction in the \tilde{X} state. The analysis of an e-e band proves to be a challenge. Its appearance is quite different from that of the a-e bands. The rotational structure of the a-e band is very congested since the entire band spans only 4 cm^{-1} . However, the e-e band spans more than 7 cm^{-1} with a concomitant decrease in line density. Most of the observed rotational lines in the e-e band belong to Q branches. The P and R branches do exist but the intensities are much weaker than the corresponding Q branches. The details of analysis will be presented.

RC11

10 min 11:28

JAHN-TELLER AND SPIN-ORBIT COUPLING IN THE 2E GROUND STATE OF CF_3O AND CF_3S

TIMOTHY A. BARCKHOLTZ AND TERRY A. MILLER, *Laser Spectroscopy Facility, Department of Chemistry, The Ohio State University, Columbus, Ohio 43210.*

The electronic spectra of the $\tilde{A}^2A \leftrightarrow \tilde{X}^2E$ transition of the CF_3O and CF_3S radicals are complex because of Jahn-Teller activity in the 2E ground states. Proper analyses of the spectra require the inclusion of both Jahn-Teller coupling and spin-orbit coupling. For CF_3O , the couplings are similar in magnitude whereas in CF_3S the spin-orbit coupling clearly dominates, although Jahn-Teller coupling cannot be ignored. The analysis of the emission spectra have included first-order and second-order Jahn-Teller coupling constants in each of the three Jahn-Teller active e modes, as well as spin-orbit coupling. Results of our analyses will be presented along with improvements to the computational program.

RC12

15 min 11:40

VIBRONIC ANALYSIS OF THE $B^2A' - X^2A''$ LASER-INDUCED FLUORESCENCE OF JET-COOLED ETHYLTHIO (C_2H_5S)

YUAN-PERN LEE, MIN-YI SHEN, AND WEN-CHING HUNG, *Department of Chemistry, National Tsing Hua University, Hsinchu, TAIWAN 30043.*

The ethylthio (C_2H_5S) radical was formed by 248-nm laser photolysis of diethyl disulfide ($C_2H_5SSC_2H_5$) or ethyl mercaptan (C_2H_5SH) in a free jet expansion. The $B - X$ fluorescence excitation spectrum was recorded in the wavelength region 398 - 440 nm. Preliminary data show that the origin lies at 23519.6 cm^{-1} with a main progression of C-S stretching (420.5 cm^{-1}). Other vibrational modes at 256.0, 861.0, 1054.6, and 1203.3 cm^{-1} were also observed for the B state. Detection of hot bands in the excitation spectrum enables assignments of three low-lying modes of the X state: 296.2, 479.9, and 672.8 cm^{-1} . Dispersed fluorescence spectra in the spectral region 410 - 520 nm revealed a main progression of C-S stretching (673 cm^{-1} with additional vibrational modes of the X state near 308, 475, 882, 1076, and 1257 cm^{-1} . Observed vibrational wavenumbers of both B and X states agree with theoretical calculations by the B3LYP/cc-PVDZ+f method (for the X state) and the MP2/DZP method (for both states).

RC13

15 min 11:57

LASER INDUCED FLUORESCENCE SPECTROSCOPY OF THE C_4H AND C_4D RADICALS

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Laser-induced-fluorescence spectra of the C_4H and C_4D radicals have been observed for the first time. The molecules were generated in a supersonic jet by an electric discharge of C_2H_2 or C_2D_2 diluted in Ar. Fourteen and thirteen vibronic bands were observed for C_4H and C_4D respectively, in the near UV region ($24000 - 25000\text{ cm}^{-1}$). The bands were assigned to the $^2\Sigma - ^2\Sigma$ or $^2\Pi - ^2\Sigma$ type, and several $^2\Sigma - ^2\Sigma$ bands were subjected to rotational analyses. The determined rotational constants for the lower state agree with those for C_4H/C_4D in the ground vibrational level in the $X^2\Sigma$ state, which were reported in a previous microwave study ^{a b}. The spin-orbit splittings in the $^2\Pi - ^2\Sigma$ bands are 16 and 12 cm^{-1} for C_4H and C_4D , respectively, leading a conclusion that the excited electronic state for the observed band system is $^2\Pi$. The present observation is consistent with a recent CASSCF study^c, which predicted the $B^2\Pi$ state with the excitation energy of 24500 cm^{-1} .

^aC.A. Gottlieb, E.W. Gottlieb, P. Thaddeus, and M. Kawamura, *Astrophys. J.* 275, 916 (1983).

^bD.R. Woodward, J.C. Person, C.A. Gottlieb, and C.A. Thaddeus, *Astrophys. J.* 333, L29 (1988).

^cA.L. Sobolewski and L. Adamowicz, *J. Chem. Phys.* 102, 394 (1995).

RD01**30 min 8:30****Ab initio study of photodissociation of several small molecules.**

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The mechanisms of photodissociation of several small molecules, including CH_3O , C_2H_2 , and O_3^- , have been studied with ab initio calculations. The CASSCF-MRSDCI approach as well as the EOM-CCSD method has been applied to study the potential energy surfaces of ground and excited electronic states. Minima on the seam of crossing have been located and the reaction coordinates from them have been analyzed using the analytical gradient method, and their roles in the photodissociation process are discussed.

RD02**15 min 9:05****EXCITATION OF COUPLED ELECTRONIC STATES**

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Coupled molecular electronic states are responsible for many complex features in observed spectra. For example, Rydberg-valence interactions are well known to cause significant anomalies in the photoabsorption spectra of O_2 , NO and N_2 .^a It is possible to explain such complexity using a coupled-channel Schrödinger equation (CSE) model based on the techniques of atomic scattering theory.^b Such a model indicates that dramatic changes to the appearance of the optical spectrum occur when the relative magnitudes of the transition moments into the coupled states are altered.

We extend the CSE model to describe non-optical processes such as dissociative charge transfer (DCT) and electron energy loss (EEL) spectra merely by changing the transition moments to reflect the changed excitation mechanism. The dramatic changes in EEL spectra for allowed transitions into coupled states as the scattering conditions are changed can be easily explained by introducing the concept of a generalized transition moment.^c

^aH. Lefebvre-Brion and R. W. Field, *Perturbations in the Spectra of Diatomic Molecules* (Academic, Orlando, 1986).

^bF. H. Mies, *Mol. Phys.* **14**, 953-972 (1980).

^cM. Dillon, M. Kimura, R. J. Buenker, G. Hirsch, Y. Li, and L. Chantryanpong, *J. Chem. Phys.* **102**, 1561-1568 (1995).

RD03**15 min 9:22****AB INITIO CALCULATION OF BiN SPECTRUM: CAN $^5\Sigma^+$ - $^1\Sigma$ TRANSITIONS BE OBSERVED?**

ALEKSEY B. ALEKSEYEV, H.-P. LIEBERMANN, G. HIRSCH AND R.J. BUENKER, *Theoretische Chemie, Bergische Universität, D-42097 Wuppertal, Germany*.

Potential energy curves of the ground $\text{XO}^+(^1\Sigma^+)$ state and a number of the low-lying excited states of BiN are calculated employing the relativistic CI method based on effective core potentials. Fifteen outer electrons of bismuth and five of nitrogen were treated explicitly in the computational procedure. The calculated spectroscopic constants (T_e , r_e , and ω_e) are in good agreement with the available experimental results, as is the ground state D_e value, computed to be 28400 cm^{-1} . The two lowest-lying excited Λ - S states are found to be $a^3\Sigma^+$ and $b^5\Sigma^+$ and have essentially shifted minima with respect to the ground state due to the opening of the π^4 valence shell. The a_20^- state is predicted to lie 1740 cm^{-1} higher than a_11 . It is shown that the b_10^+ state has a strongly perturbed potential curve with a shoulder on its repulsive limb due to an avoided crossing between the $b^5\Sigma^+$ and $^3\Pi$ states. This result explains the increase in its B_v constant with v' found experimentally.^a A number of other bound states and avoided crossings are indicated in the calculations which may be of relevance in future experimental investigations of this system. The radiative lifetimes are also calculated for electric-dipole-allowed transitions between the states considered and analyzed in terms of Λ - S contributions.

^aR. Breidohr, K. D. Setzer, O. Shestakov, E. H. Fink, and W. Zyrnicki, *J. Mol. Spectrosc.* **166**, 471 (1994).

RD04

10 min 9:39

The Electronic Structure of LiAl and its Positive Ion

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Abstract

The ground state ($1\Sigma^+$) and several low lying excited states (including the $1\Sigma^-$, $3\Sigma^-$, 1Π , and 3Π) of LiAl are characterized by MCSCF, MRCI, and ACPF techniques using large correlation consistent basis sets. The ground state of LiAl has a calculated vibrational frequency of 308 cm^{-1} , a bond length of 2.83 Angstroms, and a dissociation energy of 0.805 eV. All of the excited states of LiAl studied, thus far, dissociate to ground state Al($2P$) atom and to a first excited state Li($2P$) atom. These excited states have vertical excitation energies within 15000 cm^{-1} of the ground state. The positive ion of LiAl and its excited states have been included in this study and are characteristic of a positively charged Li atom electrostatically bound to a neutral Al atom.

RD05

10 min 9:51

Ab-Initio Study of Several Low-Lying States of YN

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The bond lengths, bond energies, and vibrational frequencies of the ground and several low-lying states of the YN molecule, calculated using GVB, CASSCF, and MRCI techniques will be reported. A comparison will be made with the appropriate states of ScN. The ground state of YN ($1\Sigma^+$) and ScN ($1\Sigma^+$) are strongly bound at each level of calculation and the ordering of the low-lying states is similar in both species. The nature of the bonding in the $1\Sigma^+$, $3\Sigma^+$, 3Δ , and two different 3Π states of YN will be discussed.

RD06

10 min 10:03

GROUND-STATE SPLITTING OF Am^{2+} IN CaF_2

SCOTT R. BROZELL AND RUSSELL M. PITZER, *Department of Chemical Physics, The Ohio State University, Columbus, OH 43210.*

The energy-level splittings of the $5f^7$ nominal $^8S_{7/2}$ ground-state of Am^{2+} in an octahedral site of CaF_2 were studied using *ab initio* quantum chemical methods. The CaF_2 host was modeled with a large finite cluster of ions which approximate the Madelung potential of the crystal lattice^a. The potential energy curve for the symmetric stretch of the nearest-neighbor fluoride ions was calculated. The actinide dopant was treated with relativistic core potentials and Gaussian double-zeta basis sets.

^aN. W. Winter, M. Ross and R. M. Pitzer *J. Phys. Chem.* **94**, 1172 (1990).

Intermission

RD07

15 min 10:30

JAHN-TELLER EFFECT IN VCl_4

Ke Zhao and Russell M. Pitzer

The Jahn-Teller effect on the 2E ground state of VCl_4 has been investigated using *ab initio* restricted Hartree-Fock, CI calculations, and spin-orbit CI calculations with relativistic core potentials and gaussian double zeta plus polarization basis sets. The effects of the Jahn-Teller active E vibration were studied by computing the energy when opposite angles were simultaneously changed. The minimum energy occurs with opposite angles opened by 2.8° , and is 97.4 cm^{-1} below the tetrahedral energy. Closing these angles by 2.6° corresponds to a saddle point on the surface which is 4.3 cm^{-1} higher in energy.¹

Vibronic energies were calculated using generalized Born-Oppenheimer approximations and a harmonic oscillator expansion. The lowest energy level was found to be 6 cm^{-1} below the T_d energy. Thus this is an example of the dynamic Jahn-Teller case.

The two-dimensional magnetic moment surface along the E vibrational coordinates was calculated and fitted to a second order equation. The magnetic moment of each vibronic state was then calculated using the vibronic wavefunction and the magnetic moment equation. The results showed a sizable effect of the vibronic interactions on the g factors. The two g factors are calculated to be 1.994 and 1.934 without the vibronic coupling, but change to 1.985 and 1.879 with the vibronic coupling effect considered. The calculated g factors agree with some but not all of the electron spin resonance data.

1. K. Zhao and R. M. Pitzer, *The Proceedings of the 50th Ohio State University International Symposium on Molecular Spectroscopy*, 252(1995).

RD08**15 min 10:47****Ab Initio Calculation of $U(BH_4)_4$**

Zhiyong Zhang, Russell M. Pitzer, *Department of Chemical Physics, The Ohio State University, Columbus, OH 43210.*

SCF calculations with relativistic core potential and double zeta Gaussian basis set, followed by spin-orbit CI calculations, were carried out on $U(BH_4)_4$. The ground state is found to be E state in double group notation, in agreement with experiments. The low lying f- > f transitions are calculated and results are compared with experiments and ligand field theory assignments.

RD09**15 min 11:04****VARIATIONAL QUANTUM MONTE CARLO CALCULATIONS INCLUDING SPIN-ORBIT COUPLING**

Heinz-Jürgen Flad, Michael Dolg and Alok Shukla, *Max-Planck-Institut für Physik komplexer Systeme (Aussenstelle Stuttgart), D-70569 Stuttgart, Germany.*

Electron correlation and relativistic effects play an important role in the chemistry and physics of heavy elements. Relativistic pseudopotentials do not only offer a possibility to reduce the computational effort by means of elimination of the core electrons, but also represent an efficient and reliable way to incorporate scalar relativistic as well as spin-orbit dependent terms in the Hamiltonian. Using this type of valence-only model Hamiltonian we performed variational Quantum Monte-Carlo calculations for atoms and small molecules of heavy elements. Electron correlation was accounted for by Jastrow factors which depend explicitly on the inter-electronic distances. The influence of dynamical correlation on the fine-structure of heavy atoms was investigated. In order to check the accuracy of our valence-only approach, we compare the results to those of fully relativistic all-electron configuration interaction calculations.

RD10**15 min 11:21**

MOLECULAR MULTICENTER INTEGRALS OF SPHERICAL GAUSSIAN FUNCTIONS BY GENERALIZED GRADIENT OPERATOR METHOD, L.-Y. CHOW CHIU, Department of Chemistry, Howard University, Washington DC 20059, AND M. MOHARRERZADEH, Natural Sciences and Mathematics Department, Bowie State University, Bowie, MD 20715.

The spherical Laguerre Gaussian type function (LGTF) centered at nucleus A , $L_n^{1/2}(ar_A^2)\mathcal{G}_{lm}(r_A)\exp(-ar_A^2)$, can be generated by operating on the Gaussian exponential, $\exp(-ar_A^2)$, with a generalized gradient operator, $\mathcal{G}_{nlm}(\nabla_A)$.¹ Through the vector coupling of the gradient operators, the Talmi coefficient of transforming the product of two LGTFs, one centered at A and the other centered at B , into a linear combination of the products of two different LGTFs, one centered at P (center of mass of A and B) and the other made of the internuclear coordinates, has been obtained. Multicenter molecular integrals of the overlap, the Coulomb repulsion, the spin-spin interaction and the spin-other-orbit interaction can be evaluated analytically. The integral results are simpler than those obtained by Fourier transform convolution theorem.²

1. G. Fieck, *Theoret. Chim. Acta* **54**, 323 (1980).

2. M. Moharrerrzadeh and L.-Y. Chow Chiu, *J. Chem. Phys.* **104**, 616 (1996).

RD11

15 min 11:38

THE VIBRATIONAL FREQUENCIES OF HALOSILYLENES HSiX (X = F, Cl, Br), KALVIN J. GREGORY and ROGER S. GREV, Department of Chemistry, The University of Kentucky, Lexington, KY 40506.

There are a number of ambiguities and curiosities found in the published Si-H stretching vibrational frequencies of the ground states, \tilde{X}^1A' , and first excited singlet states, \tilde{A}^1A'' , of the halosilylenes HSiF, HSiCl, and HSiBr. Here we have investigated these molecules using self-consistent field, SCF, configuration interaction including all single and double excitations, CISD, and triple excitations, CISDT, and complete active space, CAS-SCF, quantum mechanical methods. For the ground and first excited triplet states, all these methods give similar results, but for the excited singlet states, only the CASSCF results are believable.

RD12

15 min 11:55

AB INITIO STUDIES OF THE Ar-NO⁺ CATIONIC COMPLEX USING HIGH LEVEL CALCULATIONS, A.M. BUSH, T.G. WRIGHT, Chemistry Dept., The University, Highfield, Southampton, SO17 1BJ, United Kingdom. V. SPIRKO, J. Heyrovský Institute of Physical Chemistry, Academy of Sciences of the Czech Republic, 182 23 Prague 8, Dolejskova 3, Czech Republic.

Ab initio calculations using the cc-pVDZ and cc-pVTZ basis sets are used to calculate the geometry of the Ar-NO⁺ complex using MP2, MP4(SDQ), CCSD(T) and QCISD(T) calculations. In all cases, it is shown^a that the complex is T-shaped with an Ar-N-O bond angle of 105°, which corresponds to a Jacobi angle of *ca.* 65°, with the argon atom on the nitrogen side. Additionally, potential energy surfaces are calculated for the MP2, MP4(SDQ) and CCSD(T) methods, using the same two basis sets, and anharmonic frequencies are derived from these. The values derived therefrom are compared with those previously calculated using the MP2 method^b, and those derived from a selected CI approach^c.

(a) T.G. Wright, Chem. Phys. Lett. (submitted).

(b) T.G. Wright, P. Hobza and V. Spirko, J. Chem. Phys., **100**, 5403-5410 (1994).

(c) J.-M. Robbe, M. Bencheikh and J.-P. Flament, Chem. Phys. Lett., **210**, 170-174 (1993); I. Fourré and M. Raoult, Chem. Phys. **198**, 1-11 (1995).

RE01

15 min 1:30

NEAR-DISSOCIATION THEORY ANALYSIS FOR THE DISSOCIATION ENERGY AND VIBRATIONAL EXTRAPOLATION FOR $\text{Ba}^+\text{-Ar}$

Robert J. Le Roy, *Guelph-Waterloo Centre for Graduate Work in Chemistry, University of Waterloo, Waterloo, Ontario N2L 3G1, Canada.*

Panov *et al.*^a recently reported dispersed emission and both low and high resolution $\text{B}^2\Pi - \text{X}^2\Sigma^+$ excitation spectra for the $\text{Ba}^+\text{-Ar}$ complex. Their analysis of those data involved merging a high quality electronic structure calculation with an RKR potential for the well. However, while reasonable dissociation energies were obtained, their approach does not readily provide any estimate of the uncertainties. The present paper shows that equivalent (or better) results, which also include realistic estimates of the extrapolation uncertainties, can be obtained by simply applying near-dissociation expansion (NDE) fits directly to the experimental data.

^a S.I. Panov, J.M. Williamson and T.A. Miller, *J. Chem. Phys.* **102**, 7359 (1995)

RE02

15 min 1:47

title: Microwave spectroscopy of the long-range $\text{Ne}\cdots\text{Ne}^+$ ($^2\Pi$) ion

authors: Alan Carrington, David I. Gammie, Andrew M. Shaw and Susie M. Taylor
Department of Chemistry, University of Southampton, Southampton SO17 1BJ, UK.

We have observed the first state-to-state resonant electronic spectrum of Ne_2^+ . We use an ion-beam technique to study the ion, in which a nozzle beam of neutral neon molecules is ionised by an electron beam and the resulting molecular ion beam is studied by microwave spectroscopic methods. This ionisation technique results in significant population of the near-dissociation levels of the molecular ion, so that a sensitive state-selective electric field dissociation method can be used to detect the spectra. 68 transitions have been observed spanning the frequency range 6-170GHz, both single photon and by a microwave-microwave double-resonance technique. We have measured the Zeeman splitting produced by a small axial magnetic field for many of the lines, which enables us to determine the values of the total angular momentum J involved in each transition and also the effective g factors for the two levels involved. Using this information and that from double-resonance experiments, we have begun to construct an experimental energy level diagram for the molecule. The measured g factors suggest that the description of Ne_2^+ lies somewhere between Hund's cases (c) and (e).

RE03**15 min 2:04**

PHOTODISSOCIATION SPECTROSCOPY OF Ca^+ -RARE GAS COMPLEXES, S.H. PULLINS, C.T. SCURLOCK, J.E. REDDIC, AND M.A. DUNCAN Department of Chemistry, University of Georgia, Athens, GA 30602

Weakly bound complexes of the form $\text{Ca}^+\text{-RG}$ ($\text{RG} = \text{Ar, Kr, Xe}$) are prepared in a pulsed nozzle/laser vaporization cluster source and studied with mass-selected resonance enhanced photodissociation spectroscopy. The Ca^+ ($^2\text{P}_{1/2}$) atomic resonance line is the chromophore giving rise to the molecular spectra in these complexes. Vibrationally resolved spectra are measured for these complexes in the corresponding $^2\Pi\text{-X}^2\Sigma^+$ molecular electronic transition. These spectra are red-shifted from the atomic resonance line, indicating that each complex is more strongly bound in its excited $^2\Pi$ state than it is in the ground state. Vibronic progressions allow determination of the excited state vibrational constants: $\text{Ca}^+\text{-Ar}$, $\omega_e' = 165 \text{ cm}^{-1}$; $\text{Ca}^+\text{-Kr}$, $\omega_e' = 149 \text{ cm}^{-1}$; $\text{Ca}^+\text{-Xe}$, $\omega_e' = 142 \text{ cm}^{-1}$. Extrapolation of the excited state vibrational progressions, and combination with the known atomic asymptotes and spectral shifts, leads to determination of the ground state dissociation energies: $\text{Ca}^+\text{-Ar}$, $D_0'' = 700 \pm 100 \text{ cm}^{-1}$ (0.09 eV); $\text{Ca}^+\text{-Kr}$, $D_0'' = 1400 \pm 150 \text{ cm}^{-1}$ (0.17 eV); $\text{Ca}^+\text{-Xe}$, $D_0'' = 2300 \pm 150 \text{ cm}^{-1}$ (0.29 eV). The spin-orbit splitting in the $^2\Pi_{1/2,3/2}$ state for these complexes is larger than expected by comparison to the Ca^+ atomic value.

RE04**15 min 2:21**

PHOTOIONIZATION SPECTROSCOPY OF IONIC METAL DIMERS: CuLi AND AgLi , L.R. Brock, A.M. Knight, J.E. Reddic, J.S. Pilgrim and M.A. Duncan, Department of Chemistry, University of Georgia, Athens, GA 30602

Electronic spectra are observed for the heteronuclear metal dimers CuLi and AgLi , with resonant one-color two-photon ionization (R2PI). The dimers are produced in a pulsed supersonic molecular beam by laser vaporization of either a copper or silver rod coated with a thin, vacuum deposited lithium metal layer. A total of twelve excited electronic states for CuLi and seven for AgLi are observed. Analysis of the vibrational progressions yields ground and excited state frequencies, anharmonicities and dissociation energies for both CuLi and AgLi . In addition, selected vibronic bands are rotationally resolved, giving bond lengths for CuLi and AgLi ($r_0'' = 1.73$ and 2.08 \AA respectively). The bond lengths for CuLi and AgLi are significantly shorter than those in the homonuclear diatomics Li_2 and Cu_2 or Ag_2 . Dissociation energies in the heteronuclear dimers are also much greater than the mean of the corresponding homonuclear dimer values. These trends indicate that ionic bonding plays a leading role in the ground state bonding.

RE05**15 min 2:38**

THE (1+1) REMPI SPECTROSCOPY OF $\text{Rg}\cdot\text{NO}$ ($\text{Rg}=\text{Ar, Kr}$) VIA THE $\tilde{\text{A}}^2\Sigma^+$ ELECTRONIC STATE. A. M. BUSH, J. M. DYKE, P. MACK, D. M. SMITH, AND T.G. WRIGHT, Chemistry Department, The University, Highfield, Southampton, SO17 1BJ United Kingdom.

The one-colour REMPI spectrum of $\text{Ar}\cdot\text{NO}$ and $\text{Kr}\cdot\text{NO}$ have been recorded where the resonances are occurring in the $\tilde{\text{A}}^2\Sigma^+$ (3s) Rydberg state, which is localised on the NO moiety. Structure is seen which initially suggests assignment to intermolecular vibrational modes; however, in fact it appears that this structure is associated with rotation of the whole complex, essentially about the intermolecular axis. Rotation of the complex about the other rotational axes is not resolved in this work, but causes broadening of the observed lines.

RE06

15 min 2:55

EXPLANATION OF WHY THE RESONANT STRUCTURE SEEN IN THE (1+1) REMPI SPECTRUM OF Kr·NO VIA THE $\tilde{A}^2\Sigma^+$ STATE APPEARS IN THE Kr^+ MASS CHANNEL AS WELL AS THE $Kr\cdot NO^+$ MASS CHANNEL, A.M. BUSH, J. M. DYKE, P. MACK, D.M. SMITH, and T.G. WRIGHT, Chemistry Dept., The University, Highfield, Southampton, SO17 1BJ United Kingdom.

The (1+1) REMPI spectrum of the $\tilde{A}^2\Sigma^+$ state of $Kr\cdot NO$ appears not only in the $Kr\cdot NO^+$ channel, as would be expected, but also in the Kr^+ channel; this is despite the fact that the ionization energy of Kr is such that three photons of the laser light used would need to be absorbed in order to produce these ions. Four mechanisms are considered: Two presented previously by Miller¹ and two novel mechanisms. All the mechanisms have pros and cons, and these will be detailed in the talk.

(a) J. C. Miller, J. Chem. Phys., **90**, 4031-4036 (1989).

RE07

15 min 3:12

O₂ PHOTOABSORPTION IN THE 40950-41300 CM⁻¹ REGION: NEW HERZBERG BANDS, NEW ABSORPTION LINES, AND IMPROVED SPECTROSCOPIC DATA, T. G. Slanger, D. L. Huestis, and P. C. Cosby, Molecular Physics Laboratory, SRI International, Menlo Park, CA 94025; H. Naus and G. Meijer, Dept. of Molecular and Laser Physics, University of Nijmegen, Toernooiveld 1, 6525 ED Nijmegen, The Netherlands

The technique of cavity ring-down (CRD) spectroscopy is particularly useful for measuring absorptions of very weak optical transitions. We have in this manner investigated the 40950-41300 cm⁻¹ region in O₂, where only absorption in the O₂($A^3\Sigma_u^+ - X^3\Sigma_g^-$) 11-0 band had been previously identified. Five new bands have been discovered in this range - the $A^3\Delta_u - X^3\Sigma_g^-$ 12-0 and 13-0 bands, the $c^1\Sigma_u^- - X^3\Sigma_g^-$ 17-0 and 18-0 bands, and the $A^3\Sigma_u^+ - X^3\Sigma_g^-$ 12-0 band. The origins of the F₁ and F₂ components of the latter lie only 7 cm⁻¹ below the lowest dissociation limit, and 14 lines have been identified. No F₃ levels were observed; apparently all are above the dissociation limit. The high instrumental sensitivity of the CRD technique has allowed observation of weak lines of the A-X 11-0 band, and 12 of the 13 branches have been identified and their intensities measured. A very low upper limit has been set on the intensity of the thirteenth branch, Q₁₃. We find 106 unidentified lines in the region, the stronger ones (18) lying in the vicinity of lines of the A-X 11-0 band. The weaker ones (88) are spread throughout the spectral region, up to and even beyond the O₂ dissociation limit, and probably have their origin in transitions to very weakly bound O₂ states, which may have atmospheric significance. These weaker lines have intensities that are typically 1-5% of the strong A-X 11-0 band lines.

Intermission

RE08

10 min 3:45

LASER INDUCED FLUORESCENCE STUDY OF THE EFFECT OF PERTURBATIONS ON THE RADIATIVE LIFETIMES AND COLLISIONAL RELAXATION OF THE CO($a^1\Sigma^+$, $v=31$ AND 35) STATES*, G. ZIKRATOV, D. W. SETSER, Department of Chemistry, Kansas State University, Manhattan, KS 66502; N. SADEGHI, Laboratoire de Spectrometrie Physique, Universite Joseph Fourier-Grenoble I, B. P. 87, 38402 St. Martin d'Heres, France.

The CO($a^1\Sigma^+$, $v=31,35$) valence and CO($b^1\Sigma^+$, $v=0,1$) Rydberg states were selectively excited from the CO($a^3\Pi$) metastable molecules that were produced in a CO₂+He discharge afterglow. Excitation was accomplished by a 10 ns dye laser pulse and fluorescence was observed through a 0.3 m monochromator. The extended vibrational progressions of the CO(a') and CO(b) states back to CO($a^3\Pi$), and the fluorescence waveforms from particular bands were studied to understand the effect of the interaction between the CO(a') and CO(b) states on their radiative lifetimes, vibrational band intensities, and the collisional transfer rates in He and Ar bath gases.

The radiative lifetimes of the CO(b , $v=0,1$) states were measured as 55 ± 5 ns and those of the deperturbed CO(a' , $v=31,35$) states as 3 ± 1 μ s. Intensity borrowing by the CO(a') states results in a mixed character of their Franck-Condon factors, as demonstrated by the band intensities of the emission spectra. The rotational quantum number dependent interaction gives strongly decreasing perturbation strengths with increasing J , which affects the rotational line intensities within a given vibrational band. Analysis of the electronic and rotational relaxation rates among the CO* states at this energy and estimations of the corresponding rate constants in He will be presented. It was demonstrated that collisional transfer rates between the interacting CO(a' , $v=35$ and b , $v=1$) and CO(a' , $v=31$ and b , $v=0$) pairs were not the fastest relaxation rates.

* Supported by US National Science Foundation

RE09

15 min 3:57

THE EMISSION CONTINUUM OF ELECTRON EXCITED MOLECULAR HYDROGEN, X. LIU, Jet Propulsion Laboratory, Pasadena, CA 91109, D. E. SHEMANSKY, University of Southern California, Los Angeles, CA 90089, H. ABGRALL and E. ROUEFF, Observatoire de Paris, Section de Meudon, 92195 Meudon Cedex, France.

Photo-excitation of hydrogen molecule from the X $^1\Sigma_g^+$ state to the B $^1\Sigma_u^+$, C $^1\Pi_u$, B' $^1\Sigma_u^+$, and D $^1\Pi_u$ states and subsequent emission to the dissociation continuum is the primary destruction mechanism of H₂ in interstellar clouds. We have recently calculated continuum emission profiles of B $^1\Sigma_u^+$ - X $^1\Sigma_g^+$, C $^1\Pi_u$ - X $^1\Sigma_g^+$, B' $^1\Sigma_u^+$ - X $^1\Sigma_g^+$, and D $^1\Pi_u$ - X $^1\Sigma_g^+$ transitions of H₂. Synthetic spectra based on the calculated profiles are in excellent agreement with high-resolution electron-impact induced emission spectra obtained at 100 eV. An improved intensity calibration standard and dissociation yields of the Lyman and Werner continua produced by both electron and photon impact excitation will be presented.

RE10

15 min 4:14

HIGH-RESOLUTION SPECTROSCOPY USING A CCD ARRAY DETECTOR: THE $A \rightarrow X$ SYSTEM IN OH, J. TELLINGHUISEN, Department of Chemistry, Vanderbilt University, Nashville, TN 37235.

The $A \rightarrow X$ transition in OH is studied in emission from a Tesla discharge through Ar containing a small amount of water vapor. This system is used as a test case for investigating the capabilities of a CCD array detector (Photometrics CCD9000, 1024x256 pixels 25 μm on a side) in application to problems of high-resolution spectroscopy. The high information content of these spectra enables the 0-0 band to be least-squares fitted to a nonlinear model containing some 40 parameters, including 9 line-shape parameters. The combination of high signal-to-noise and large dynamic range makes possible the observation of OD lines amongst the OH lines, even though the natural abundance of OD is only 1/7000 that of OH. For example, in the residuals plot of Fig. 1 the prominent negative peaks near 3071.6, 3072.6, 3073.2, 3073.6, 3074.7, 3075.0, and 3076.0 \AA are all readily assignable to OD. When this species is included in the fit model, it should be possible to assess its abundance to better than 10% relative reliability — a remarkable testament to the potential for this technology.

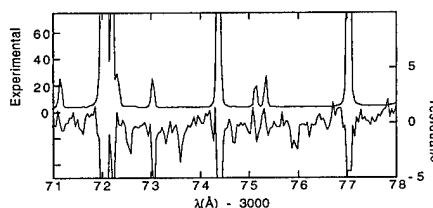


Fig. 1. Segment of the $A \rightarrow X$ spectrum of OH recorded at high resolution using a CCD array detector. The peaks in the experimental spectrum (top) extend to ~ 500 in this region. The lower spectrum shows the scaled residuals from a least-squares fit of the spectral region 3070-3103 \AA .

RE11

15 min 4:31

A study of core non-penetrating Rydberg States of CaF

H. Ma, *Department of Physics, Tsinghua University, Beijing 100084, China*, Y. M. Liu, J. Li
and W. F. Polik, K. L. Cunningham, R. W. Field, *Department of Chemistry, MIT, 77 Mass. Ave., Cambridge, MA 02139*

In a double resonance ionization experiment, calcium monofluoride $v=1$ $n^*=14-18$ Rydberg states were observed using a jet-cooled molecular beam and a time of flight mass spectrometer. Spectra were recorded via $C^2\Pi_{3/2}$ $v=1$ intermediate states of both e and f symmetry and $J=1.5 - 13.5$. A preliminary assignment revealed that the strong features around integer n^* were from the core non-penetrating f states. In the range of $n^*=14-16$, all seven components of each f complex were assigned. Term values were fitted to an effective f complex Hamiltonian which included coupling effects due to the core dipole and quadrupole moments^a.

^a J. K. G. Watson, *Mol. Phys.*, vol.81 p.277 (1994)

RE12

10 min 4:48

ON THE LEAST-SQUARES FITTING OF CORRELATED DATA: *A PRIORI VS A POSTERIORI* WEIGHTING, J. TELLINGHUISEN, Department of Chemistry, Vanderbilt University, Nashville, TN 37235.

One of the methods in common use for analyzing large data sets is a two-step procedure, in which subsets of the full data set are first least-squares fitted to preliminary sets of parameters, and the latter are subsequently merged to yield the final parameters. The second step of this procedure is properly a correlated least-squares fit and requires the variance-covariance matrices from the first step to construct the weight matrix for the merge. There is, however, an ambiguity concerning the manner in which the first-step variance-covariance matrices are assessed, which leads to different statistical properties for the quantities determined in the merge. The issue is one of *a priori vs a posteriori* assessment of weights, which is an application of what was originally called *internal vs external consistency* by Birge^a and Deming^b. In the present work the simplest case of a merge fit — that of an average as obtained from a global fit vs a two-step fit of partitioned data — is used to illustrate that only in the case of *a priori* weighting do the results have the usually expected and desired statistical properties: normal distributions for residuals, *t*-distributions for parameters assessed a posteriori, and chi-square distributions for variances.

^aR. T. Birge, *Phys. Rev.* **40**, 207-227 (1932).

^bW. E. Deming, "Statistical Adjustment of Data," Dover, New York, 1964.

RE13

15 min 5:00

THE $B(1/2^2P_{3/2}) \rightarrow X(1/2^2\Sigma^+)$ TRANSITION IN XeBr

JASON O. CLEVENGER, Department of Chemistry, MIT, Cambridge, MA 02139; and
JOEL TELLINGHUISEN, Department of Chemistry, Vanderbilt University, Nashville, Tennessee 37235.

The $B(1/2^2P_{3/2}) \rightarrow X(1/2^2\Sigma^+)$ transition in XeBr was recorded in high resolution, using a CCD array detector to record spectra from Tesla discharge sources containing isotopically pure ^{136}Xe with $^{81}\text{Br}_2$ or $^{79}\text{Br}_2$ ^{ab}. The high signal/noise capabilities of the detector permitted the measurement of discrete vibrational structure in this system, which has normally been treated as a purely bound-free transition. The assignments comprised 119 $v'-v''$ bands for $^{136}\text{Xe}^{81}\text{Br}$ and 86 for $^{136}\text{Xe}^{79}\text{Br}$, spanning $v' = 0-33$ and $v'' = 0-16$. The van der Waals ground state was analyzed through fits to the customary polynomials and to near-dissociation expansions. Franck-Condon calculations were used to locate the *X*-state potential on the internuclear axis relative to the *B* state, which was modeled as a Rittner potential. The following fundamental spectroscopic constants (units cm^{-1} , for $^{136}\text{Xe}^{81}\text{Br}$) were obtained from the analysis: $T_e' = 35\,863.2$, $\omega_e' = 135.72$, $\omega_e x_e' = 0.32$, $\omega_e'' = 25.7$, $\omega_e x_e' = 0.62$. The ground state has a dissociation energy $D_e'' = 254 \pm 2 \text{ cm}^{-1}$ and supports 24 bound vibrational levels.

^aJason O. Clevenger and Joel Tellinghuisen *Chem. Phys. Lett.* **231**, 515 December 1994.

^bJason O. Clevenger and Joel Tellinghuisen *J. Chem. Phys.* **103**(22), 9611 December 1995.

RE14

15 min 5:17

THE $B \rightarrow X$ TRANSITION IN XeI, D. RADZYKEWYCZ AND J. TELLINGHUISEN, Department of Chemistry, Vanderbilt University, Nashville, TN 37235.

The $B (1/2^2P_{3/2}) \rightarrow X (1/2^2\Sigma^+)$ transition in XeI (2385-2490 Å) has been recorded at high resolution for the single isotopomer $^{136}\text{Xe}^{127}\text{I}$, using a Tesla discharge source and a CCD array detector. The high signal-to-noise capabilities of the detector make it possible to measure the discrete vibrational structure in this system for the first time. The assignments consist of 86 $v'-v''$ bands spanning 15 upper-state levels (assigned as $v' = 3-17$) and 17 lower-state levels (tentatively assigned as $v'' = 0-16$). A vibrational analysis yields the following spectroscopic constants (cm^{-1}): $\Delta T_e = 40\,047.8$, $\omega_e' = 110.6$, $\omega_e x_e' = 0.217$, $\omega_e'' = 24.0$, $\omega_e x_e'' = 0.66$. A fit of the data to a near-dissociation expansion indicates that the X state has a dissociation energy (\mathcal{D}_e) of $267 \pm 3 \text{ cm}^{-1}$ and supports 28 bound vibrational levels. However, there are signs that our lowest observed v'' level may not be $v'' = 0$, so these values should be considered lower limits. Trial-and-error Franck-Condon calculations are used to locate the B - and X -state potential curves relative to each other, fixing the X -state R_e at a value 0.7-0.8 Å larger than that for the B state.

When the spectra of the rare-gas halides were first investigated over 20 years ago, it appeared that only in XeF and XeCl could discrete bands be discerned in the dominant $B \rightarrow X$ and $D \rightarrow X$ systems. The emission spectra of all other RgX species were modeled as bound-free. Now it appears that faint violet-degraded band structure in the short-wavelength wings of these systems, of the sort measured and analyzed here, may be more the rule than the exception. With the completion of the present work, all four of the XeX species have now been vibrationally characterized, similar work having been completed recently for XeBr^a.

^aJ. O. Clevenger and J. Tellinghuisen, *J. Chem. Phys.*, **103**, 9611-9620 (1995).

RE15

10 min 5:34

Laser Spectroscopy of the $A^3\Pi_{1u} \leftarrow X^1\Sigma_g^+$ System of I_2 in the 11650-12300 cm^{-1} region

TOKIO YUKIYA, NOBUO NISHIMIYA AND MASAO SUZUKI, *Department of Electronic Engineering, Tokyo Institute of Polytechnics, Iiyama 1583, Atsugi City, 243-02 Kanagawa, Japan.*

The Doppler limited electronic absorption spectrum in the $A^3\Pi_{1u} \leftarrow X^1\Sigma_g^+$ system was measured in the 11650-12300 cm^{-1} region using a Ti:sapphire ring laser (Coherent 899-21) pumped by an argon ion laser (Coherent Innova 90). The Q-branch lines of $J = 10$ to 100 belonging to the $v' \leftarrow v'' = (29 \sim 31)' \leftarrow 0''$, $(21 \sim 30)' \leftarrow 1''$ and $(22 \sim 31)' \leftarrow 2''$ progressions were assigned. The hyperfine splittings of these lines could not be resolved. The wavelength measurements were done using a wavelength-meter (Anritu MF9630A) with an accuracy of $\pm 0.5 \text{ ppm}$. Using a least squares fitting procedure, the spectroscopic constants of ν_Q^0 , $B_{vf}' - B_v''$, $D_{vf}' - D_v''$ and $H_v' - H_v''$ were determined. The standard deviations were smaller than 0.003 cm^{-1} . By using the Dunham's coefficients of the X -state reported by Tromp and LeRoy (1), the spectroscopic constants of T_v' , B_{vf}' , D_{vf}' and H_{vf}' suitable for $v' = 21' \sim 31'$ of the A -state were determined by a global least squares fits. The rotational constant of B_{vf}' at the $v' = 21$ agreed with that reported by Ishikawa et al. (2) within the standard error, while the discrepancy of 0.1 cm^{-1} was found at the value of T_v' .

(1) J. W. TROMP AND R. J. LE ROY, *J. Mol. Spectrosc.* **109**, 352-367(1985).

(2) T. ISHIKAWA, H. TAKEKAWA AND K. OBI, *J. Mol. Spectrosc.* **159**, 443-457(1993).

OBSERVATION OF LUMINESCENCE SPECTRA OF KrD RYDBERG MOLECULE AT LOW (40K) TEMPERATURE

A. A. PELMENEV, E. B. GORDON, V. V. KHMELENKO, M. V. MARTYNNENKO, E. A. POPOV, *Institute for Energy Problems of Chemical Physics, 142432, Chernogolovka, Moscow Region, Russia.*

The luminescence spectra of KrD Rydberg molecule in spectral range from 400 nm to 800 nm in gas phase at low temperatures (40K) were observed for the first time by means of original experimental technique. In this method two gas jets were intersected over the surface of superfluid helium (temperature 1.5K, pressure of helium vapor 10 torr). Gas mixture of He with 1-5frequency electrodeless discharge. The resulting luminescent jet was introduced in a helium cryostat and crossed by a stream of H₂ or D₂ molecules to produce RgH or RgD. First experiments with Kr and D₂ were carried out. A number of bands observed in the luminescence spectra were assigned to KrD extensively studied by Dabrowski et al. ^a. The most pronounced bands observed at 515 nm and 773 nm originate from 4d state and correspond to transitions to 5p states. Transitions from the np complexes were also identified but their intensity were much weaker. Near 483 nm there was rather broad band assigned to transitions from nf complexes. The luminescence spectra of nitrogen molecules and ions, and CN radicals at such low temperatures were also studied and a number of peculiarities in the spectra were observed. These results will be presented as well.

^aI. Dabrowski, D. A. Sadovskii, *Molecular Physics*, 81(2), 291, (1994).

RF01

15 min 1:30

ANALYSIS OF THE $Q_1(1)$ IMPURITY NEXT NEAREST NEIGHBOR (NNN) PAIR SPECTRUM IN SOLID PARAHYDROGEN AND NON-RESONANT VIBRON HOPPING, YU ZHANG, TERESA J. BYERS, DAVID P. WELIKY, AND TAKESHI OKA, Department of Chemistry, Department of Astronomy and Astrophysics, and Department of Physics, The University of Chicago, Chicago, IL 60637-1403.

The $Q_1(1)$ ($v = 1 \leftarrow 0, J = 1 \leftarrow 1$) rovibrational spectrum of the $J = 1$ ortho- H_2 impurities in solid para- H_2 , which was recorded earlier in our laboratory using a difference frequency spectrometer^{a,b}, shows an intricate structure due to intermolecular interactions between pairs of $J = 1$ H_2 molecules. More than 260 lines were observed using tone burst frequency modulation. We presented our assignment of the nearest neighbor (nn) pair transitions last year at this meeting. In this paper we present the assignment of the nnn pair transitions based on the vibrational ground state ($v = 0$) energy levels of nnn pairs determined by Statt, Hardy, and Jochemsen^c. From the assignment we are able to locate all of the 18 energy levels in the excited state except for the symmetric $|00\rangle$, $|22_{\pm}\rangle$ and antisymmetric $|10\rangle$ levels. All of the 9 energy levels in the ground state have been located including the $|00\rangle$ and $|22_{\pm}\rangle$ levels that had previously been missing^c. The assignment of the symmetric and antisymmetric states provides us the accurate frequency of the vibron hopping between the nnn pair. We were surprised to find that the frequency is a factor of 3 higher than $1/8$ of the hopping frequency for nn pair as expected from approximate $1/R^6$ dispersion type dependence of the hopping. A model considering non-resonant hoppings of the $v = 1$ exciton via $J = 0$ H_2 is applied to explain this anomaly.

a. M. C. Chan, M. Okumura, C. M. Gabrys, L. W. Xu, B. D. Rehfuss, and T. Oka, Phys. Rev. Lett. **66**, 2060 (1991).

b. K. E. Kerr, T. Momose, unpublished results.

c. B. W. Statt, W. N. Hardy, and R. Jochemsen, Can. J. Phys. **58**, 1326 (1980).

RF02

10 min 1:47

NEW INFRARED TRANSITIONS OF SOLID PARAHYDROGEN IN THE SPECTRAL REGION 7900 - 9900 cm^{-1}

M. MENGEL, B. P. WINNEWISSER AND M. WINNEWISSER, *Physikalisch-Chemisches Institut, Justus-Liebig-Universität, Heinrich-Buff-Ring 58, D-35392 Giessen.*

In our most recent measurements of infrared transitions of solid parahydrogen with low ortho impurities, using a White-type external multireflection system ^a for a sample path length of 38 cm, we have detected new extremely weak features in the spectral region 7900 - 9900 cm^{-1} . Among them are the single transition

- $Y_{1\leftarrow 0}(0)$ at 7991.85 (1) cm^{-1}

and the double transitions

- $Q_{1\leftarrow 0}(0) + Q_{1\leftarrow 0}(0)$ at 8306.0 (1) cm^{-1}
- $U_{1\leftarrow 0}(0) + Q_{1\leftarrow 0}(1)$ at 9407.67 (5) cm^{-1}
- $Q_{1\leftarrow 0}(0) + S_{1\leftarrow 0}(0)$ at 9747.8 (1) cm^{-1}
- $U_{1\leftarrow 0}(1) + Q_{1\leftarrow 0}(0)$ at 9837.34 (5) cm^{-1} .

The $Y_{1\leftarrow 0}(0)$ transition is the second transition with $\Delta J = 8$ observed in a molecular spectrum after the $Y_{0\leftarrow 0}(0)$ transition ^b and is even weaker than the latter by an appreciable factor. Intensity parameters will be reported for all of these transitions. The data were taken at a sample temperature of 12.3 K.

^aR. Steinhoff, K. V. S. R. M. Winnewisser, Appl. Optics **32**, 6577-6581 (1993).

^bR. A. Steinhoff, B. P. Winnewisser and M. Winnewisser, Phys. Rev. Lett. **73**, 2833 - 2836 (1994).

RF03

15 min 1:59

EXTENDED OBSERVATION AND ANALYSIS OF THE FIRST OVERTONE SPECTRUM OF SOLID PARAHYDROGEN

M. MENGEL, B. P. WINNEWISSER AND M. WINNEWISSER, *Physikalisch-Chemisches Institut, Justus-Liebig-Universität, Heinrich-Buff-Ring 58, D-35392 Giessen.*

The first overtone spectrum of solid parahydrogen with various low ortho impurity levels has been studied in detail using a White-type external multireflection system ^a. For the $Q_{2\leftarrow 0}(0)$ transition we have observed the fully resolved threefold splitting due to the crystal field effect. Furthermore we have obtained a rich satellite spectrum associated with the transitions $Q_{2\leftarrow 0}(0)$ and $Q_{2\leftarrow 0}(1)$ at different ortho- H_2 contents revealing information about the ortho- H_2 pair interaction in the second vibrationally excited state of the hydrogen molecule. A preliminary analysis and assignment of these satellite transitions will be presented. Another point of study was the spectral region around 8300 cm^{-1} , where the double transitions of the type $Q_{1\leftarrow 0}(n) + Q_{1\leftarrow 0}(n')$ ($n, n' = 0, 1$) are located. The most remarkable features here are the $Q_{1\leftarrow 0}(1) + Q_{1\leftarrow 0}(1)$ transition which consists entirely of fine structure and the $Q_{1\leftarrow 0}(0) + Q_{1\leftarrow 0}(0)$ transition for which no mechanism has so far been suggested. Finally the thermal shift of all of the above mentioned transitions was investigated by lowering the sample temperature from the triple point at 13.8 K down to 6.5 K while taking spectral data. The influence of the change of temperature on the line positions, line widths and line strengths of solid hydrogen will be discussed.

^aR. Steinhoff, K. V. S. R. M. Winnewisser, *Appl. Optics* 32, 6577-6581 (1993).

RF04

15 min 2:16

INFRARED SPECTROSCOPIC STUDY OF CARBON CLUSTERS TRAPPED IN SOLID PARAHYDROGEN

TAKAMASA MOMOSE, MASAOKI MIKI, TOMONARI WAKABAYASHI, AND TADAMASA SHIDA, *Division of Chemistry, Graduate School of Science, Kyoto University, Kyoto 606-01, JAPAN.*

Recently solid parahydrogen is shown to be a promising medium for matrix-isolation spectroscopy.^a Availing of several salient features of the new matrix, we are studying molecules of chemical interest such as free radicals. In the present work, we report infrared spectra of small carbon clusters trapped in solid parahydrogen. Carbon clusters were produced by laser vaporization of a carbon rod placed inside the optical cell. The second harmonic of a Q-switched Nd:YLF laser was used for ablation. The observed infrared spectrum showed the presence of small carbon clusters such as C_3 , C_5 and C_9 in a parahydrogen crystal at 4.8K. A detailed analysis of the spectrum reveals that these clusters are not rotating freely but are strongly hindered by surrounding hydrogen molecules.

^aT. Oka *Annu. Rev. Phys. Chem.*, **44**, 299 (1993); D. P. Weliky, T. J. Byers, K. E. Kerr, T. Momose, R. M. Dickson, and T. Oka, *Appl. Phys. B* **59**, 265 (1994).

RF05

15 min 2:33

Laser induced fluorescence and beam depletion spectroscopy of K atoms attached to large hydrogen clusters

C. Callegari, F. Stienkemeier ^a, J. Higgins, and G. Scoles, *Department of Chemistry, Princeton University, Princeton, New Jersey 08544.*

Hydrogen clusters are produced in a supersonic expansion and are subsequently doped with K atoms by passing the beam through a pick-up cell containing K vapor at a pressure of about 10^{-2} Pa. Optical $4^2P_{3/2} \leftarrow 4^2S_{1/2}$ spectra for K atoms are obtained in two different ways:

- a) by Laser Induced Fluorescence (LIF)
- b) by measuring the Beam Depletion (BD) induced by the laser using a hot wire surface ionization detector located downstream of the LIF collector

For hydrogen clusters the LIF spectra are two orders of magnitude lower in intensity as compared to those obtained using He clusters, due to quenching. The LIF spectra consist of several narrow features near the gas phase potassium doublet and a second series of very broad features located about 300-600 cm^{-1} to the blue. The BD spectrum shows surprising differences from the LIF. The blue-shifted features are still present, but most of the absorption is now located under a prominent envelope (about 200 cm^{-1} broad) centered on the gas phase doublet. These differences will be discussed at the meeting.

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RF06

15 min 2:50

TRANSITION-METAL MONOSILONYLS [M(SiO), M = Cu, Ag, Au, V]: ESR AT 4 K, A.P. WILLIAMS, R.J. VAN ZEE, AND W. WELTNER, JR., Department of Chemistry, University of Florida, Gainesville, FL 32611.

M(SiO) molecules were prepared by laser vaporization of the metal and solid SiO during condensation of neon and/or argon matrices at 2-4 K. ESR (9 GHz) spectra were measured and the analyses compared with the known results for the corresponding monocarbonyls. Cu and Ag^a formed linear $^2\Sigma$ molecules, but Au(SiO) is a non-linear $S = 1/2$ molecule, in contrast to linear Au(CO)^b. V(SiO) has a $^4\Sigma$ ground state as compared to $^6\Sigma$ in the monocarbonyl^c. Other first-row transition-metals did not form silonyls visible via ESR.

^aT. Mehner, H. Schnöckel, M.J. Almond, and A.J. Downs, *J. Chem. Soc., Chem. Commun.* 117 (1988); J.H.B. Chenier, J.A. Howard, H.A. Joly, B. Mile, and P.L. Timms, *ibid*, 581 (1990).

^bP.H. Kasai and P.M. Jones, *J. Am. Chem. Soc.* **107**, 6385 (1985).

^cR.J. Van Zee, S.B.H. Bach, and W. Weltner, Jr., *J. Phys. Chem.* **90**, 583 (1986).

RF07

15 min 3:07

COOPERATIVE EFFECTS IN OPTICAL AND ESR SPECTROSCOPY OF NITROGEN ATOMS ISOLATED BY SOLIDIFICATED HELIUM, E.B. GORDON, R.E. BOLTNEV, V.V. KHMELLENKO, M.V. MARTYENKO, A.A. PELMENEV AND E.A. POPOV, Institute for Energy Problems of Chemical Physics (branch), 142432 Chernogolovka, Moscow Region, Russian Federation.

The heavy guest particles embedded to superfluid helium can cause its solidification¹. The so-called Impurity Helium Solid Phase (IHSP) being stable then up to $T=7\text{K}$ shows the regular arrangement of the impurities with their reliable isolation by helium atoms. The feasibility of previously excited species capture to IHSP may be achieved. So metastable $\text{N}(^2\text{D})$ atoms display extremely long-lived, more than 10^4 s, luminescence. Their radiative decay turns out to be caused solely by excimer-like state formation with accidentally neighboring heavy particle². That was proved for $\text{N}(^2\text{D})\text{-Rg}$ pairs ($\text{Rg} \equiv \text{Ne, Ar, Kr, Xe}$) by both spectra shapes and emission lifetimes observed. For $\text{N}(^2\text{D})\text{-N}_2$ state the comparison of atomic $\text{N}(^2\text{D}-^4\text{S})$ and rovibronic $\text{N}(^2\text{D})\text{-N}_2(v=0) \rightarrow \text{N}(^4\text{S})\text{-N}_2(v=1)$ spectra evidences their excimer nature as well³.

The distances between neighbour N atoms in IHSP, 1 nm, are small enough for cooperative bulk magnetic effects appearance. ESR experiments with $\text{N}(^4\text{S})$ atoms show the effects of either magnetic alignment or spin-exchange narrowing.

-
1. E.B. Gordon, V.V. Khmelenko, A.A. Pelmenov, E.A. Popov and O.F. Pugachev, Chem. Phys. Lett. **155**(3), 301-304 (1989).
 2. R.E. Boltnev, E.B. Gordon, V.V. Khmelenko, A.A. Pelmenov, I.N. Krushniskaya, M.V. Martynenko, E.A. Popov and A.V. Shestakov, Chem. Phys. **189**(2), 367-382 (1994).
 3. R.E. Boltnev, E.B. Gordon, V.V. Khmelenko, M.B. Martynenko, A.A. Pelmenov, E.A. Popov, and A.F. Shestakov, J. Chim. Phys. **92**(2), 362-383 (1995).

Intermission

RF08

15 min 3:40

ABSOLUTE INFRARED ABSORPTION INTENSITIES OF LIQUID MIXTURES OF CH_3CN AND H_2O , John E. Bertie and Zhida Lan. Department of Chemistry, University of Alberta, Edmonton, Alberta, T6G 2G2 Canada.

Absolute infrared absorption intensity spectra have been obtained between 4500 and 700 cm^{-1} for water, acetonitrile, and water-acetonitrile mixtures over the whole range of compositions. The spectra of the imaginary molar polarizability, α_m'' , have been calculated for each mixture. The α_m'' spectrum of an ideal mixture is the sum of the α_m'' spectra of the components weighted by the mole fraction of the component. The measure of integrated intensity that has the greatest theoretical significance is the area under a band in the spectrum of $\tilde{\nu}\alpha_m''$. The area under band j in this spectrum is designated C_j . Thus, for each band, a graph of C_j versus mole fraction is linear if the mixture is ideal. Such graphs have been constructed for the acetonitrile-water system. The observed non-linearities have been analyzed to obtain the number of free and hydrogen-bonded acetonitrile molecules at each composition, and the number of free, O-H---O bonded, and O-H---N bonded, OH groups at each composition.

RF09

15 min 3:57

The FTIR Study of the UV Irradiation of Amorphous and Crystalline Acetyl Chloride

Brad Rowland and Wayne Hess, *Battelle Pacific Northwest Laboratories, PO Box 999, Richland, WA. 99352, Mail Stop K2-14.*

The UV irradiation of amorphous and crystalline acetyl chloride samples at 10K produces dimer complexes of ketene and HCl molecules. We use infrared spectroscopy to study the vibrational spectra of the ketene-HCl complexes formed by the elimination of HCl within the 3 μ m thick acetyl chloride film. Ab-Initio calculations are used to facilitate the interpretation of the infrared spectra and to obtain optimized geometries for the complexes. The formation of ketene-HCl complexes is reversible at temperatures that exceed 50K. Rate information and an activation energy are obtained for the reverse reaction of the most abundant ketene-HCl conformation.

RF10

15 min 4:14

The Interaction of Strong Hydrogen-Bonding Molecules with the Surface of Nano-sized Crystalline Ice Clusters.

Lance Delzeit and J. Paul Devlin

Department of Chemistry, Oklahoma State University, Stillwater, OK 74078

The adsorption of strong hydrogen-bonding molecules to the surface of ice nanocrystals causes the surface and/or subsurface modes of the cluster to be shifted to lower frequency. These shifted modes form a triplet with band centers at the characteristic frequencies of the bulk modes. This effect will be explained in terms of the acidic and basic groups of the adsorbate molecules and the spatial relationship of these groups to the surface groups of the clusters. The IR difference spectra of the adsorbate-coated minus the bare clusters will be compared to the bulk amorphous and bulk crystalline deposits. Some of the strong adsorbates that will be considered are H_2S , HCN, and SO_3 . A comparison between strong and weak hydrogen-bonding adsorbates will be made using differences in the IR spectra.

CF_4 has previously been used in identifying the "disordered" nature of the ice surface. Its spectrum is known to have a distinctive structure, in the intensity and shape of the T/L splitting of the antisymmetric stretch, which is indicative of the vertical roughness and lateral disorder of the surface. It will be used again in identifying the surface "disorder" of the adsorbate-coated clusters. This will give further insight into the character of the surface of the adsorbate-coated clusters.

A new ice surface-localized mode has been observed. It can tentatively be assigned to one of two possible modes: 1) the symmetric stretch of the dangling-hydrogen water molecule, or 2) the globally symmetric O-H stretch mode activated by surface polarization. Arguments for each will be addressed.

RF11

15 min 4:31

COMPARATIVE STUDIES OF THE TRIPLET MONOCYCLIC AROMATIC DIAZINES UNDER PRESSURE, I. Y. CHAN, W. WANG, Department of Chemistry, Brandeis University, Waltham, MA 02254

We report a zero-field optically detected magnetic resonance (ODMR) study under high pressure for triplet pyrimidine in benzene, pyrazine in benzene and in *p*-dichlorobenzene, and *s*-tetramethylpyrazine in durene. For azaromatics, the size of the non-bonding orbital on the N atoms is smaller than that of an aromatic C-H fragment, therefore under moderate pressure, the interaction of a non-bonding electron with the neighboring atoms in a crystalline matrix is still attractive in nature. Thus pressure will stabilize the n -electron, resulting in an up-shift in energy of a $n\pi^*$ state. This leads to a decrease in the spin-orbit coupling contribution to D in $n\pi^*$ triplets of pyrimidine and pyrazine. Other contrasting behaviors are explained by the difference in crystalline packing. There is a large change in D and a multiplet splitting under high pressure for tetramethylpyrazine. These are ascribed to the presence of a pseudo Jahn-Teller interaction in this molecule.

RF12

15 min 4:48

THE EFFECT OF EXTERNAL PRESSURE ON THE HIGH SPIN TO LOW SPIN TUNNELING RATE OF A Fe(II) SPIN CROSSOVER SYSTEM, W. WANG, I. Y. CHAN, Department of Chemistry, Brandeis University, Waltham, MA 02254.

For a class of Fe(II) coordination compounds, the spin state is temperature dependent^a. A compound that is in the high spin state (HS) above a thermal transition temperature may cross over to the low spin state (LS) when it is at low temperature. Based on the "light-induced excited spin state trapping (LIESST)" mechanism^b, a spin crossover compound may be excited from the LS to HS at low temperatures and the HS to LS relaxation process may be studied. Early experiments^b showed that this relaxation follows a non-Arrhenius behavior at low temperatures. It may be considered a tunneling process along the Fe and ligand bond symmetric stretching normal coordinate. The effect of external pressure on the spin relaxation rates of $[\text{Fe}(4-\{(6\text{-methyl})\text{-}2\text{-pyridyl}\}\text{-}3\text{-aza-}3\text{-butenyl})_3\text{amine}](\text{PF}_6)_2$ or $[\text{Fe}(\text{mepy})_3(\text{tren})](\text{PF}_6)_2$ doped in its Zn analog is measured at 10K and 50K. The external pressure on the sample is obtained by using a diamond anvil cell. The high spin state is prepared by exciting the sample with 514 nm laser pulses generated from a YAG pumped optical parametric oscillator (OPO) and the HS to LS relaxation rate is measured by probing the recovery of the absorption of the low spin state with a HeNe laser. Pressure increases the energy gap between the two spin states by several hundred wavenumbers, leading to a spectacular enhancement of the tunneling rate. Our results show a change of eight orders magnitude in the relaxation time constant between ambient pressure and 20 kbar, from $\sim 0.1\text{ s}^{-1}$ to $\sim 6 \times 10^6\text{ s}^{-1}$. A theoretical interpretation will be presented.

^aPhilipp Gütlich, Andreas Hauser, and Hartmut Spiering, *Angew. Chem. Int. Ed. Engl.* **33**, 2024 (1994).

^bAndreas Hauser, Andreas Vef, and Peter Adler, *J. Chem. Phys.* **95**, 8710 (1991)

RF13

15 min 5:05

HIGH PRESSURE STUDIES OF J-AGGREGATES, I.Y. CHAN, Department of Chemistry, Brandeis University, Waltham, MA, 02254; **M. LINDRUM^a,** Fachbereich Physik, Free University, Berlin, Germany.

The spectral shift of J-bands under high pressure up to 60 kbar has been investigated for J-aggregates of different cyanine dyes. Under conditions where no J-band can be observed at normal pressure, J-aggregates are formed at higher pressure. A red shift of absorption upon increasing pressure was found with a linear dependence of line position on pressure. The results can be explained by a change of dipolar coupling of monomer molecules in the aggregate due to decreasing center-to-center distances. The different pressure slopes of various aggregates are interpreted from their different aggregate structures. The monomer absorption is also red shifted under pressure, but the pressure dependence is quite different and can be described by a solvent shift. From the linear dependence, the dipole-dipole coupling energy J can be determined with a simple theory. The general applicability and limitations of this method are discussed.

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RF14

15 min 5:22

PENETRATION DEPTHS OF PHOTOMOBILIZED F ATOMS FROM A SANDWICH EXPERIMENT, Institut für Experimentalphysik, Freie Universität Berlin, Arnimallee 14, D-14195 Berlin, Germany; C. Bressler, M. Dickgießer, and N. Schwentner

Electronic excitation of an insulator leads in general to a significant rearrangement of the lattice which can induce even a displacement of atoms like in the color center formation. For even stronger changes in the equilibrium coordinates an atom in the excited center can gain significant energy thus being photomobilized. The distance where it comes at rest again due to dissipation of its kinetic energy corresponds to its penetration depth and a mean range can be derived. Exceptionally large penetration depths were predicted for photomobilized F atoms in a rare gas lattice [1] and a new direct and reliable technique will be presented for the determination of the mean range [2]. F₂ molecules are dissociated in a doped Ar layer of typical 5nm thickness by means of synchrotron radiation with a photon energy of 10.15 eV. F atoms gain a kinetic energy of about 4.2 eV and part of them can cross a spacer layer of pure Ar and some of them will reach the interface between the Ar spacer and the Kr substrate. The thickness of the Ar spacer is varied with monolayer accuracy from 0 up to 10 nm and the penetration depths are derived from the decreasing number of F atoms at the interface with increasing spacer thickness for a complete dissociation of F₂. The intensity of the Kr₂⁺ F⁻ emission, which is characteristic for the interface, delivers the amount of F atoms and the sensitivity is enhanced considerably by using energy transfer from excitons of the Kr substrate. Indeed, larger penetration depths with mean values corresponding to eight nearest neighbor distances are observed and the results are discussed with respect to the molecular dynamics simulations, angular distributions in the plan as system, homogeneity and ordering of the sample structure and temperature effects.

- [1] R. Alimi, R.B. Gerber, V.A. Apkarian; J. Chem. Phys., 92, 3551 (1990)
- [2] C. Bressler, N. Schwentner; Phys. Rev. Lett., 22, 648 (1996)

RF15

15 min 5:39

INFRARED SPECTROSCOPY AND PHOTOCHEMISTRY OF NITROMETHANE ADSORBED ON ALKALI HALIDE FILMS, MARGARET CULLEN, GERALD WAYTON, AND C.A. BAUMANN, Department of Chemistry, University of Scranton, Scranton, PA 18510.

Nitromethane (CH₃NO₂) was adsorbed at low temperature onto films of sublimated alkali halides. Assignment of the infrared spectrum of the adsorbed species is consistent with physisorption, as are thermal desorption isotherms (desorption activation energies of 26-32 kJ mol⁻¹). The photochemistry of the adsorbate is sensitive to surface temperature and wavelength of irradiation. None of the primary products of gas phase photolysis (CH₂O, HNO, CH₃NO, O, CH₃, NO₂) were observed, although traces of methyl nitrite (CH₃ONO) were observed. The appearance of species such as HNCO and CO as a result of irradiation indicates that fragment migration and rephotolysis may play a major role in these reactions.

RG01**10 min 1:30**

PRESSURE BROADENING OF AMMONIA INVERSION STATES FROM 5 - 30 K, D. R. WILLEY, P. DENARDO, T. TYSZKA, and R. TIMLIN, Department of Physics, Allegheny College, Meadville, PA 16335.

We present helium pressure broadening measurements obtained using a collisionally cooled cell for the $J = 1, K = 1$ and $J = 2, K = 2$ microwave inversion transitions of ammonia at kinetic temperatures of 5 - 30 K. Experimental results will be compared to calculations derived from recent He - NH₃ potential surfaces.

RG02**15 min 1:42**

VARIABLE TEMPERATURE PRESSURE BROADENING OF H₂S.

C. D. BALL, J. M. DUTTA, T. M. GOYETTE, P. HELMINGER, F. C. DE LUCIA

Linewidths of H₂S pressure broadened by He, H₂, N₂, and O₂ have been measured between 100 and 600 K. Two rotational transitions of the ground vibrational state were studied in an equilibrium cell. Deviations from the exponential temperature dependence of the broadening parameter are discussed. Comparisons are made between these results and the results of similar studies involving SO₂, H₂O, HDO, and HNO₃.

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Address of Dutta: Department of Physics, North Carolina Central University, Durham, NC 27707.

Address of Helming: Department of Physics, University of South Alabama, Mobile, AL 36688.

RG03**10 min 1:59**

THE VARIABLE TEMPERATURE PRESSURE BROADENING OF H₂S IN COLLISION WITH HYDROGEN
D. C. FLATIN, C. BALL, AND F. C. DE LUCIA

Pressure broadening cross sections for the $2_{2,0} \leftarrow 2_{1,1}$ rotational transitions of hydrogen sulfide (H₂S) in collision with hydrogen (H₂) have been measured between 12 and 500 K. Measurements below 40 K were made using the collisional cooling technique, while measurements at higher temperatures were made in an equilibrium cell. Comparisons of these data with earlier measurements of the $1_{1,0} \leftarrow 1_{0,1}$ transition will be made as well as comparisons to measured cross sections of hydrogen sulfide in collision with helium (He). The data analysis techniques and experimental apparatus are described.

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RG04

15 min 2:11

FURTHER INVESTIGATIONS OF THE BrO ROTATIONAL SPECTRUM

Edward A. Cohen and Holger S. P. Müller, *Jet Propulsion Laboratory, California Institute of Technology, Pasadena, California 91109.*

The rotational spectrum of the $^2\Pi_{1/2}$ state of BrO has been observed for the first time in selected regions between 80 and 520 GHz. Observations of the $^2\Pi_{3/2}$ state in its ground and first excited vibrational state have been extended to over 600 GHz and improved. In addition, we have observed the $^2\Pi_{3/2} v = 2$ and $^2\Pi_{1/2} v = 1$ states of normal BrO and Br ^{18}O in natural abundance in its $^2\Pi_{3/2}$ state. Transitions arising from the $^2\Pi_{3/2} v = 1$ and $^2\Pi_{1/2} v = 0$ states of Br ^{18}O have been observed in a slightly enriched sample. Analysis of these new data along with previously published spectra has resulted in improvements in the precision of previously determined parameters as well as the first determination of others. In particular, the equilibrium mechanical constants have been more precisely determined. The quadrupole coupling in the $^2\Pi_{1/2}$ state, the Fermi contact term for the Br nucleus, and the nuclear spin rotation constant have been derived. The effects of isotopic substitution have been used to determine the electron spin rotation coupling constant. The details of the analysis will be presented and the significance of the parameters will be discussed.

RG05

15 min 2:28

THE ν_1 and ν_2 BANDS OF DOBr AND THE ROTATIONAL SPECTRA OF THE $v_2 = 1$ AND $v_3 = 1$ STATES

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The ν_1 and ν_2 bands of DOBr centered near 2673.2 and 853.4 cm^{-1} respectively have been observed at 0.006 cm^{-1} resolution. The ν_1 band is perturbed by an anharmonic resonance ($\Delta K_a = 0$) with $3\nu_3 + \nu_2$. In addition, the millimeter spectra arising from the $v_2 = 1$ and $v_3 = 1$ states have been observed. All rotational and vibrational spectra from both bromine isotopic species have been fitted with a single calculation. The perturbation in the ν_1 band has been well described. Equilibrium rotational and centrifugal distortion constants have been determined. The equilibrium structure has been derived from the DOBr and HOBr rotational constants. The harmonic force field has been calculated and will be compared with that of HOCl and with those derived from *ab initio* calculations. Changes in quadrupole coupling with the BrO stretch and DOBr bend have been determined.

RG06

15 min 2:45

SPECTROSCOPY OF BROMINE DIOXIDE, OBrO

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The rotational spectra of O⁷⁹BrO and O⁸¹BrO have been studied for the first time in selected regions between 88 and 627 GHz in the (000), (010), and (020) states. OBrO is a rather asymmetric prolate rotor ($\kappa = -0.824$) with a large dipole moment and a bending mode of *ca.* 310 cm⁻¹. This results in a rich spectrum, permitting a large range of *J*'s (1 - 61) and *K_a*'s (0 - 14) to be observed. The splittings caused by the electronic and nuclear spins are substantially larger than those of the related OClO. Rotational, centrifugal distortion, electron and nuclear spin-rotation, spin-spin, and nuclear quadrupole coupling constants have been determined. Centrifugal distortion terms for the ϵ 's and some of the hyperfine constants have also been determined. The molecular structure and the harmonic force constants have been derived. Results from gas phase infrared and visible spectroscopy will be presented briefly.

Intermission

RG07

15 min 3:20

Microwave spectrum and geometry of cyanogen N-oxide, NCCNO

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The microwave spectrum of cyanogen N-oxide (NCCNO) has been measured using a new pulsed jet cavity Fourier transform microwave spectrometer, which incorporates automated frequency scanning. The sample was synthesized by gas phase thermolysis of dicyanofuroxan at 550°C, and subsequently diluted to ~ 1 % in the Ne backing gas. The spectrum is that of a linear top; it is complicated by hyperfine splittings due to the two ¹⁴N nuclei. Several isotopomers have been observed in natural abundance, and accurate rotational, centrifugal distortion and ¹⁴N nuclear quadrupole coupling constants have been obtained. Several geometries (*r*₀, *r*_s, *r*_{L,ε}) have been determined.

Several molecules related to NCCNO have been found to exhibit quasi-linearity to a greater or lesser extent. These include HCNO, NCNCS, and NCNCO. It was thus conceivable, that NCCNO also might exhibit effects of quasi-linearity. To resolve the issue, the substitution geometry and the ¹⁴N nuclear quadrupole coupling constants have been used to compare NCCNO to related molecules. To date the results indicate NCCNO to be truly linear. However, no conclusive answer is possible, since data on excited vibrational states are not available.

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^cT. Pasinszki and N. P. C. Westwood, *J. Chem. Soc. Commun.*, p. 1901 (1995)

RG08

15 min 3:37

RADIO FREQUENCY-INFRARED DOUBLE RESONANCE MEASUREMENT OF THE ELECTRIC DIPOLE MOMENT IN BEND-STRETCH COMBINATION VIBRATIONAL STATES OF HCCD

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With a small permanent electric dipole moment due to differences in zero point motion between hydrogen and deuterium, monodeuteroacetylene, HCCD, is particularly well-suited for studying changes in the dipole moment upon vibrational excitation. In fact, for several normal modes, the change in dipole moment accompanying excitation of one quantum of vibration is larger than the ground state moment. We have used radio frequency-infrared double resonance to directly measure the Stark shift of the $J = 1$ ℓ -doublet splitting in four vibrational states of HCCD. New results were obtained for two C-H stretch plus bend combination states. For the combination with the C-D bend, $\nu_1 + \nu_4$, $q_\ell = 132.289(6)$ MHz and $\mu = 0.046627(33)$ D, while for the combination with the C-H bend, $\nu_1 + \nu_5$, $q_\ell = 107.263(4)$ MHz and $\mu = 0.031385(22)$ D. Our measurements on the two bending fundamentals, ν_4 and ν_5 , were combined with earlier molecular beam electric resonance ^a and microwave ^b results to provide electric field calibration. Additionally, it appears that infrared spectra involving the $\nu_1 + \nu_4$ state have not previously been reported. Our data allow us to provide preliminary measurements for the rotational constant in this state and for the band origin of the $\nu_1 + \nu_4 - \nu_4$ hot band, namely $B = 0.9892$ cm⁻¹ and $\nu_0 = 3331.46$ cm⁻¹.

^aM. D. Marshall, and W. Klemperer, *J. Chem. Phys.* 81, 2928 (1984).

^bK. Matsumura, T. Tanaka, Y. Endo, S. Saito, and E. Hirota, *J. Phys. Chem.* 84, 1793 (1980).

RG09

10 min 3:54

THE JET PROPULSION LABORATORY SUBMILLIMETER, MILLIMETER AND MICROWAVE SPECTRAL LINE CATALOG

HERBERT M. PICKETT, R. L. POYNTER, E. A. COHEN, M. L. DELITSKY, J. C. PEARSON and H. S. P. MÜLLER, *Jet Propulsion Laboratory, California Institute of Technology, Mail Stop 183-301, 4800 Oak Grove Dr., Pasadena, CA 91109*.

The Jet Propulsion Laboratory Submillimeter, Millimeter and Microwave Spectral Line Catalog is an on-line computer accessible data base of atmospheric and astrophysical molecules with transitions in the 0 to 10,000 GHz frequency range. The current fourth edition of the catalog contains 298 species and 1,448,151 lines. The information listed for each spectral line includes the frequency with its estimated error, the intensity, the lower state energy and the quantum number assignment. The catalog has been constructed by using theoretical least squares fits of published spectral lines to accepted molecular models. The resulting predictions and their error estimates are based on the fitted parameters and their covariances. The catalog is continuously expanded and updated as new data appears. The catalog and the analysis programs used in its generation are available via anonymous ftp at spec.jpl.nasa.gov or on the world wide web at <http://spec.jpl.nasa.gov>.

RG10**10 min 4:06**

MEASUREMENTS OF THE MICROWAVE SPECTRUM, STRUCTURAL PARAMETERS, AND QUADRUPOLE COUPLING FOR METHYL RHENIUM TRIOXIDE, S. M. SICKAFOOSE, P. WIKRENT, B. J. DROUIN, AND S. G. KUKOLICH, Department of Chemistry, University of Arizona, Tucson, AZ 85721

The $J = 1 \leftarrow 0$, and $2 \leftarrow 1$ transitions for six isotopomers of methyl rhenium trioxide were measured using a Flygare-Balle type, pulsed-beam, Fourier-transform spectrometer with a heated nozzle system. The observed hyperfine structure splittings due to the ^{185}Re and ^{187}Re quadrupole coupling interactions are significantly smaller in this complex than for $\text{HRe}(\text{CO})_4$. The Re-C and Re-O bond lengths are compared with the corresponding solid-state values obtained from neutron diffraction work.

RG11**15 min 4:18**

MICROWAVE MOLECULAR STRUCTURE MEASUREMENTS FOR TETRACARBONYL DIHYDRO OSMIUM, A CLASSICAL DIHYDRIDE, S. G. KUKOLICH, S.M. SICKAFOOSE AND S.M. BRECKENRIDGE, Department of Chemistry, The University of Arizona, Tucson, AZ 85721

Microwave rotational spectra for six isotopomers of $\text{H}_2\text{Os}(\text{CO})_4$ were measured in the 4-12 GHz range using a Flygare-Balle-type spectrometer. The 18 rotational constants from these isotopomers were used to determine eight structural parameters describing the gas-phase structure of this complex. This near-octahedral complex has C_{2v} symmetry and the dipole moment lies along the c-principal axis for the normal isotopomer. The distance between H atoms, obtained directly from experimental structural parameters, is $r_{\text{HH}} = 2.40(2)\text{\AA}$. This rather long H - H distance indicates that this is clearly a "dihydride" rather than a "dihydrogen" complex. The Os - H bond lengths are $r_{\text{OsH}} = 1.72(1)\text{\AA}$. The osmium - carbonyl carbon bond lengths for axial and equatorial carbonyl groups are $r_{\text{OsC1}} = 1.96(1)\text{\AA}$ and $r_{\text{OsC3}} = 1.97(2)\text{\AA}$. Results for other structural parameters obtained using least squares fitting and the structural parameters obtained using the Kraitchman method are presented and discussed. No evidence for internal motion was observed for this complex.

RG12**15 min 4:35**

MEASUREMENTS OF THE MICROWAVE SPECTRUM, Co - H BOND LENGTH, AND ^{59}Co QUADRUPOLE COUPLING FOR THE TRANSITION METAL HYDRIDE $\text{HCo}(\text{CO})_4$, S. M. SICKAFOOSE, AND S. G. KUKOLICH, Department of Chemistry, University of Arizona, Tucson, AZ 85721

Microwave rotational transitions for the H and D isotopomers of the transition metal hydride, $\text{HCo}(\text{CO})_4$ were measured using a Flygare-Balle type spectrometer. This acidic hydride is believed to be formed from the precatalyst $\text{Co}_2(\text{CO})_8$ in hydroformylation reactions, and then lose a CO group to form the active catalyst $\text{HCo}(\text{CO})_3$. Rotational transition frequencies in the 4 - 10 GHz range were analyzed to obtain structural parameters and the ^{59}Co quadrupole coupling strength $eQq = 116.6\text{ MHz}$. The metal-hydrogen bond length obtained is $r(\text{Co-H}) = 1.57\text{\AA}$. Comparisons of this value and other structural parameters with the electron diffraction results of McNeill and Scholer^a will be made.

^aE. A. McNeill and F. R. Scholer, J. Am. Chem. Soc. **99**, 6243 (1977)

RG13**10 min 4:52****MILLIMETER AND SUBMILLIMETER SPECTROSCOPY OF CHLORINE NITRATE: THE Cl QUADRUPOLE TENSOR AND THE HARMONIC FORCE FIELD**

HOLGER S. P. MÜLLER, *Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA 91109*; PAUL HELMINGER, *Department of Physics, University of South Alabama, Mobile, AL 36688*; SIDNEY H. YOUNG, *Department of Chemistry, University of South Alabama, Mobile, AL 36688*.

The rotational spectrum of ClONO₂ has been (re-) investigated in the millimeter and submillimeter regions in the ground vibrational and first excited torsional states for both ³⁵Cl and ³⁷Cl isotopomers. A large number of *a*- and *b*-type *R*- and *Q*-branch as well as *b*-type *P*-branch transitions have been observed. This has enabled the improvement of the spectroscopic constants and the prediction of lines in the submillimeter region. Accidental near-degeneracies of rotational levels allowed the observation of a $\Delta J = 2$ transition and the precise determination of the off-diagonal quadrupole coupling constant χ_{ab} . The quartic distortion constants along with the vibrational wavenumbers and inertial defects have been used to calculate a harmonic force field. The results will be related to the molecular structure determined from an electron diffraction study and to data from related molecules such as Cl₂O.

RG14**10 min 5:04****MICROWAVE SPECTRUM, BROMINE NUCLEAR QUADRUPOLE COUPLING CONSTANTS, AND STRUCTURE OF BROMODIFLUOROMETHANE**

TERUHIKO OGATA, SUSUMU KUWANO, *Department of Chemistry, Faculty of Science, Shizuoka University, Shizuoka, 422 Japan*.

Microwave spectrum of bromodifluoromethane, CHBrF₂ (Freon FC-22B1), for the ⁷⁹Br and ⁸¹Br species has been studied by a Stark modulation spectrometer. The spectrum consists of strong *c*-type and weak *a*-type transitions. A simultaneous least-squares analysis of the observed transition frequencies gave the rotational, quartic centrifugal distortion, and bromine nuclear quadrupole coupling constants. The structural parameters has been calculated from the rotational constants for the ⁷⁹Br and ⁸¹Br species. The *r*_{F-F} distance for the ⁷⁹Br and ⁸¹Br species are 2.171843 Å and 2.171849 Å, respectively. These distance are slightly longer than the corresponding value 2.17053 Å in CHClF₂. The electronic characters of the C-Br bond have been determined from the bromine nuclear quadrupole coupling constants and are compared with those of other related molecules.

RG15**15 min 5:16****A NOVEL DESIGN MOLECULAR BEAM FOURIER TRANSFORM MICROWAVE SPECTROMETER IN THE FREQUENCY RANGE 1 TO 4 GHz**

Daniela Consalvo, Volker Storm, Helmut Dreizler, Jens-Uwe Grabow, and Ilona Merke, *Institut für Physikalische Chemie, Christian-Albrechts-Universität, Olshausenstraße 40-60, D-24098 Kiel, Germany*.

During the recent years the growing interest on heavy van der Waals complexes generates an increasing need for a spectrometer covering frequency ranges suitable for complexes with large moments of inertia. We report on a new design for a Fourier transform microwave spectrometer in the spectral region 1 to 4 GHz, especially constructed for the investigation of rotational spectra of heavy van der Waals complexes. The molecular beam microwave spectrometers used so far are based on the prototype introduced by Balle and Flygare^a. In contrast to these molecular beam spectrometers, employing a Fabry-Perot resonator working with TEM_{00q}-modes, the proposed design employs a different type of resonator operating with TE_{01q}-modes. This resonator allows for compact dimensions even at cut-off wavelengths above 0.1 m, i.e. cut-off frequencies below 3 GHz. The already fully automated spectrometer also features a coaxially oriented beam resonator arrangement, as recently introduced for Fabry-Perot resonator spectrometers^b. Details of the design, performance data and example spectra of stable molecules and complexes are given.

^aT.J. Balle and W.H. Flygare, *Rev.Sci.Instrum.* 52, 33(1981).

^bJ.-U. Grabow and W. Stahl, *Z.Naturforsch.* 45a, 1043(1990).

RH01

15 min 1:30

Doorway State Enhanced Intramolecular Vibrational Energy Redistribution In The Asymmetric Ethylenic C-H Stretch Of *Cis* Methyl Vinyl Ether

David A. McWhorter, Sam Cupp, Chung Yi Lee and Brooks H. Pate, *Department of Chemistry, University of Virginia, Charlottesville, VA 22901.*

The microwave-infrared double-resonance capabilities of an electric-resonance optothermal spectrometer have been used to assign the high resolution (5MHz) infrared spectrum of the asymmetric $=CH_2$ stretch of the *cis* conformer of methyl vinyl ether (2-methoxy propene) near 3130cm^{-1} . This vibrational state is anharmonically coupled to a near-resonant bath state by a $0.69(2)\text{cm}^{-1}$ matrix element resulting in two vibrational bands separated by $1.44(1)\text{cm}^{-1}$. The two mixed states resulting from this interaction are further coupled to other near-resonant bath states with an average matrix element of $0.006(2)\text{cm}^{-1}$. The total state density increases with total angular momentum, J , however, the Intramolecular Vibrational Energy Redistribution (IVR) rate is approximately independent on the total angular momentum quantum number. Therefore, the rotationally mediated coupling mechanisms are weaker than the anharmonic terms in the redistribution process. A two-state analysis of the strong coupling, which includes a phenomenological IVR rate constant, suggests that the IVR rate in the two mixed states is dominated by the contribution from the strongly coupled dark state.

RH02

15 min 1:47

PHOTOFRAGMENT TRANSLATIONAL SPECTROSCOPY OF HYDROGEN BONDED CLUSTERS AND CHARGE TRANSFER COMPLEXES

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Photofragment translational spectroscopy, using a pulsed-extraction time-of-flight method, has been applied to the study of kinetic energy release (KER) in weakly bound molecular complexes and clusters. The KER for cluster species manifests significant changes relative to the isolated molecule conditions, serving as a sensitive indicator of intermolecular interactions. Studies of neat hydrogen halide clusters, $(HI)_n$, reveal that the I atom fragments experience strong cage effects, in analogy with well known bulk phase phenomena, resulting in a broad, generally isotropic velocity distribution. Under the same conditions, the H atom fragment KER is largely unaltered and cage effects are not as important. However, a second, isotropic H atom velocity distribution is also detected, possibly resulting from trajectories that lead to reactive and near-reactive encounters with neighboring HI solvent species. These results can be compared to the KER of other HI containing molecular complexes. In contrast to these relatively weakly bound systems, we have also investigated KER in charge transfer (CT) complexes where the intermolecular interactions are very strong. Excitation of the CT state in $C_6H_6-I_2$ complexes leads to the production of two distinct I atom velocity distributions, reflective of the structure of the complex and the dynamics of the photochemical event. The KER of the C_6H_6 and I_2 product fragments was also measured. Wavelength resolved spectra of the C_6H_6 and C_6H_6-I chromophores also illustrate the effects of the CT process, such as the presence of rotational excitation.

RH03

15 min 2:04

THE EFFECT OF REDUCED MASS ON CROSSED BEAM ROVIBRATIONAL ENERGY TRANSFER FROM S_1 GLYOXAL (0^0 , $K' = 0$)

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Energy transfer from S_1 glyoxal (CHO-CHO) in collision with additional target gases is now added to a list of collision partners (H_2 , D_2 , He, Kr, and C_6H_{12}) previously presented. A laser is used to pump glyoxal to the $0^0, 0 \leq J' \leq 10$, $K' = 0$ level of the S_1 (1A_u) state. Rotational excitation with resolution of K states can be observed in competition with rovibrational energy transfer to the lowest frequency mode, ν_7 (also seen with K state resolution). Relative cross sections are obtained from computer simulations of the observed inelastic scattering fluorescence spectrum. A more complete picture of the relationship between rovibrational energy transfer and the reduced mass of the collision partner will be presented. These results can also be used to further establish benchmarks for the 3-dimensional quantal scattering model that has so successfully been used with past glyoxal energy transfer studies^a.

^aG.-J. Kroes, R.P.H. Rettschnick, and D.C. Clary, *Chem. Phys.* **148**, 359 (1990).

RH04

15 min 2:21

Vibrational Energy Transfer of $I_2(X, v=23$ and $v=43)$ in a Helium Free Jet Expansion

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Collision induced vibrational energy transfer of highly excited $I_2(X)$ was studied in a helium free jet expansion at about 5K. Stimulated emission pumping was used to prepare a specified vibrational state. Laser induced fluorescence of the D-X transition was then used to probe the initial and the collisionally populated states. Two vibrational levels ($v=23$, $v=42$) of $I_2(X)$ were examined in this study. Preliminary analysis suggests a weak vibrational dependence of the relaxation rate constants as well as a near temperature independent cross section when compared to room temperature data. These findings are in disagreement with the predictions of the Landau-Teller model. A more detailed analysis will be performed and the results presented. Work supported by AFOSR under grant F49620-95-1-0010

RH05

15 min 2:38

VIBRATIONAL PREDISSOCIATION OF $\text{Na}^+(\text{CH}_3\text{OH})_m$ ($m=2-7$) FROM 2.5 TO 3.0 MICRONS.

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The vibrational predissociation spectra of $\text{Na}^+(\text{CH}_3\text{OH})_m$ ($m=2-7$) clusters were recorded in the frequency range of 2.5 to 3.0 μm , corresponding to the stretch of the O-H functional group in methanol. Hydrogen bonding between two methanols, as in the case of the gas phase dimer, results in two inequivalent methanols, a proton donor and acceptor. The oscillator strength and the frequency of the proton donating methanol are strongly perturbed by the hydrogen bond. Vibrational predissociation induced through excitation of the O-H group can be used to observe the presence of hydrogen bonding. Transitions were observed around 3670 cm^{-1} for all of the cluster ions studied. This feature is attributed to methanols with the O-H groups that are not acting as proton donors in a hydrogen bond. For clusters of size $m \geq 5$, absorption features were observed below 3500 cm^{-1} which correspond to methanols with proton-donating O-H groups. The spectra will be discussed along with structural implications. For comparison, data from $\text{Cs}^+(\text{CH}_3\text{OH})_p$ cluster ions will also be briefly presented.

RH06

15 min 2:55

VIBRATIONAL PREDISSOCIATION OF $\text{Na}^+(\text{CH}_3\text{OH})_m((\text{CH}_3)_2\text{CO})_n$ ($m+n > 1$; $m, n \geq 1$) FROM 2.5 TO 3.0 MICRONS.

C. J. WEINHEIMER AND J. M. LISY, *Department of Chemistry, University of Illinois at Urbana-Champaign, Urbana, IL 61801.*

The vibrational predissociation spectra of $\text{Na}^+(\text{CH}_3\text{OH})_m((\text{CH}_3)_2\text{CO})_n$ ($m+n > 1$; $m, n \geq 1$), recorded between $3250 - 3800\text{ cm}^{-1}$, will be discussed and compared with clusters, $\text{Na}^+(\text{CH}_3\text{OH})_m$, that do not contain any acetone molecules ($n=0$). Acetone is not infrared active in this spectral region, but is capable of participating in strong hydrogen bonds with methanol. Any changes in the spectra between $\text{Na}^+(\text{CH}_3\text{OH})_m$ and $\text{Na}^+(\text{CH}_3\text{OH})_m((\text{CH}_3)_2\text{CO})_n$ can be attributed to the influence of one or more acetone molecules. As in the case of $\text{Na}^+(\text{CH}_3\text{OH})_m$ clusters, the smaller cluster sizes show an absorption around 3670 cm^{-1} , which is attributed to methanols with 'free' O-H groups. Methanols acting as proton donors to other acetone or methanol molecules absorb below 3500 cm^{-1} . The structural impact due to the presence of one or more acetones will be discussed.

RH07

15 min 3:12

MEASURING THE NUCLEAR HYPERFINE POPULATIONS IN THE GROUND ELECTRONIC STATE OF ATOMIC HYDROGEN USING VELOCITY-ALIGNED DOPPLER SPECTROSCOPY

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A variation on the technique of velocity-aligned Doppler spectroscopy has been used to measure the relative populations in the $F=0$ and $F=1$ nuclear hyperfine levels in the ground electronic state of atomic hydrogen produced in the 193 nm photolysis of HBr. This technique provides an unambiguous correlation between the H atom state distributions and the spin-orbit states of the counter fragment, i.e. $\text{Br}(^2\text{P}_{3/2})$ and $\text{Br}(^2\text{P}_{1/2})$. H atom state distributions are monitored by observing the (1+1) two-color multiphoton ionization spectrum exciting through the Lyman- α transition. Effects of small Stark fields on the observed spectra will be discussed.

RH'01

10 min 3:45

THE HIGH-RESOLUTION SPECTRUM OF WATER VAPOR BETWEEN 11300 AND 13200 CM^{-1}

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The absorption spectrum of water vapor has been recorded between 11255 and 13160 cm^{-1} , with the Fourier-transform spectrometer (Kitt-Peak, Az) at the resolution 0.012 cm^{-1} and the path length of 434 m. The line assignment has led to the determination of 448 accurate energy levels of (131), (211), (013), (230), (112), (032), (310) and (051) vibrational states belonging to the so called $3\nu + \delta$ resonance polyad. Three spectra were used in analysis: 1.5 Torr, 17 Torr and data from Ref.1. Resonance interections with (160) and (080) belonged to higher polyad were taken into account during line assignment procedure.

The complete analysis of rotational energy levels of the second decade of the interacting vibrational states has been performed. A set of 100 rotational, resonance and centrifugal distortion constants for (131), (211), (013), (230), (112), (032) and (310) vibrational states has been determined by least square fitting with r.m.s. 0.03 cm^{-1} for 415 energy levels. Line intensities were determined from peak absorption for 762 lines.

1. R.Toth, J.Mol.Spectrosc. v.166, pp.176-183 (1994).

RH'02

15 min 3:57

THE TORSION-ROTATION SPECTRUM OF D_2O_2

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The torsion-rotation spectrum of D_2O_2 has been recorded in the region from 25 to 600 cm^{-1} at a resolution (1/MOPD) of 0.003 cm^{-1} using a modified Bomem Fourier transform spectrometer. The aim of the study is to improve the torsional potential of D_2O_2 and to locate the weak oxygen-oxygen stretching fundamental which should lie amongst the torsional levels. So far, the pairs of torsional levels with $n = 0, 1$ and 2 and one of the levels with $n = 3$ have been analysed with J and K values up to 30 and 11 respectively. The current state of the analysis will be described.

RH'03

15 min 4:14

THE INFRARED SPECTRUM OF THE NO DIMER

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At last year's Symposium, we reported measurements^a of the ν_1 fundamental band (symmetric N-O stretch) of the ($^{15}\text{N}^{16}\text{O}$)₂ and $^{15}\text{N}^{16}\text{O}$ - $^{14}\text{N}^{16}\text{O}$ isotopes of the NO dimer in the 1820 to 1880 cm^{-1} region. A force field analysis of these results, together with our earlier data^b on the normal isotope, tended to cast doubt on currently accepted assignments^c of the low frequency intermolecular vibrations of this dimer, which are based on condensed phase data. (The intermolecular fundamentals in the far infrared region have never been observed in the gas phase.)

We have now obtained further NO dimer spectra in a lower frequency region, 1600-1820 cm^{-1} , using higher sample pressures (3.25 Torr) with our long-path (200 m) low temperature (92 K) absorption cell and Bomem DA3.002 FTIR spectrometer. No new resolved (NO)₂ bands were detected. However, we did obtain a high-quality band profile of the ν_5 fundamental at 1789 cm^{-1} , whose lines are broadened by predissociation to about 0.2 cm^{-1} . We also detected a number of peaks which could be Q-branches of (NO)₂ hot bands, some of which were also seen in earlier low-resolution work. The most prominent of these is a feature at 1652 cm^{-1} whose shape resembles that expected for a *c*-type Q-branch of (NO)₂. The difference band $\nu_5 \leftarrow \nu_4$ is the only possible *c*-type transition in this region, and therefore, if 1652 cm^{-1} can be so assigned, then the ν_4 out-of-plane vibration of the dimer must lie at 1789 - 1652 = 137 cm^{-1} . For comparison, Nour et al.^c put ν_4 at 94 cm^{-1} and our force fields indicated a value in the range 120-170 cm^{-1} . Further experiments are planned, including direct long-path observations in the far infrared.

^aA.R.W. McKellar, J.K.G. Watson, and B.J. Howard, *Mol. Phys.* **86**, 273 (1995).

^bA.R.W. McKellar and B.J. Howard, *Mol. Phys.* **78**, 55 (1993).

^cE.M. Nour, L.H. Chen, M.M. Strube, and J. Laane, *J. Phys. Chem.* **88**, 756 (1984).

RH'04

15 min 4:31

HIGH RESOLUTION INFRARED SPECTRA OF $^{120}\text{SnD}_4$

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High resolution FTIR spectra of the ν_2/ν_4 and the ν_1/ν_3 bands of $^{120}\text{SnD}_4$ have been measured with a Bruker 120 HR interferometer. The sample was prepared under vacuum using a two step synthesis. The ν_2/ν_4 region (425-620 cm^{-1}) was studied using a liquid He-cooled bolometer, while an MCT detector was used in the ν_1/ν_3 region (1275-1455 cm^{-1}). The resolutions of the spectra are 0.0033 cm^{-1} and 0.0024 cm^{-1} , respectively.

The ν_1/ν_3 band system has been analyzed rotationally, and a set of molecular parameters have been obtained. The measurement of the first and second stretching overtones is in progress, too. The results will be compared with those of normal stannane, SnH_4 . In the case of normal stannane vibrational localisation has been found to take place in stretching vibrational overtones. Thus the dynamical symmetry of stannane, a spherical top molecule, has been found to become that of a prolate symmetric top.

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RH'05

10 min 4:48

HIGH RESOLUTION DIODE LASER SPECTROSCOPY OF CARBONYL FLUORIDE AT STRATOSPHERIC TEMPERATURES

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The 1940 cm^{-1} band system of carbonyl fluoride, COF_2 , consisting of ν_1 (1944.6 cm^{-1}) in Fermi resonance with ν_2 (1913.8 cm^{-1}) is studied using lead-salt diode lasers tuned by temperature and current control. This molecule is important in heterogeneous chemical processes in polar stratospheric clouds and this band is used in atmospheric retrievals. The gas is contained in a multi-jacketed absorption cell and cooled to c. 210 K by a circulating fluorinated fluid which is precooled in bath of methanol and dry ice. The improved signal to noise ratio and lineshape of the diode spectra over previous Fourier Transform measurements allow further spectroscopic features to be unambiguously identified.

RH'06

15 min 5:00

HIGH RESOLUTION SPECTROSCOPY OF CH_2F_2 IN THE $3\text{ }\mu\text{m}$ REGION. THE $2\nu_8$ BAND AT 2839 cm^{-1} , Catherine L. Lugez, Alfons Weber, and Walter J. Lafferty, Molecular Physics Division, National Institute of Standards and Technology, Gaithersburg, MD 20899.

The infrared absorption spectrum of methylene fluoride (CH_2F_2) has been recorded at a spectral resolution of 0.004 cm^{-1} in the region from 2700 to 3300 cm^{-1} with the BOMEM DA3.002 Fourier transform spectrometer at NIST. The $2\nu_8$ band, centered at 2838.6 cm^{-1} , has been analyzed in detail and the analyses of the ν_1 and $(\nu_2+\nu_8)$ bands at 2948 cm^{-1} and 2943 cm^{-1} , respectively, are underway. The $2\nu_8$ band is quite perturbed, but using the non- and only slightly perturbed transitions it has been possible to obtain a least squares fit using the Watson A-reduction Hamiltonian. The ground state constants were constrained to the values reported by Carlotti, *et al.*⁽¹⁾ 1159 transitions with J and K values ranging up to 44 and 22, respectively, were used in the fit. The resulting upper state constants reproduce the experimental data (the non- and only slightly perturbed transitions) with a standard deviation of 0.00034 cm^{-1} . Full use of all observed transitions will require the inclusion of an x,y-type Coriolis interaction with the ν_6 fundamental⁽²⁾ and a z-type Coriolis coupling with the $\nu_2+\nu_8$ combination band. Work on these bands is in progress.

⁽¹⁾ M. Carlotti, G.D. Nivellini, F. Tullini, and B. Carli, *J. Mol. Spectrosc.* **132**, 158-165 (1988).

⁽²⁾ M.N. Deo, R. D'Cunha, and A. Weber, analysis reported at the 1994 Columbus meeting, paper RH08.

RH'07

15 min 5:17

CORIOLIS-DEPENDENT DIPOLE MOMENT OF THE $V_3 = 2$ STATE OF METHANE

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Stark effect of the $2\nu_3$ band of methane was studied by saturation spectroscopy using an optical cavity absorption cell and a 1.6- μm external cavity semiconductor laser. The magnitude of the determined dipole moments was dependent on the Coriolis sublevels. This dependence agreed with the higher-order dipole moment ^a,

$$\mu_\alpha \propto \ell_\beta J_\gamma + J_\beta \ell_\gamma$$

where μ is the dipole moment, ℓ are the vibrational angular momenta, J are the total angular momenta, and (α, β, γ) is (x, y, z) , (y, z, x) , or (z, x, y) components of the molecule-fixed axes.

^aM. R. Aliev, V. M. Mikhailov, and J. K. G. Watson, *J. Mol. Spectrosc.* 118, 544 (1986).

RH'08

15 min 5:34

RAMAN SPECTROSCOPY OF PHASE TRANSITIONS IN NEMATIC LIQUID CRYSTALS

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The systematic investigations of the connection of polymorphism spectral developments with thermal pre-history of nematic liquid crystal (LC) have been performed. Regularities connecting parameters of Raman bands with structural peculiarities of MBBA in different phases obtained at various rates of preliminary cooling of sample have been found [1,2]. Using these connections the conformational angles, energetic barriers between different conformers, order of nonarrangement of various phases, quantitative phase composition have been calculated. It has been made the analysis of forming mechanisms of Raman bands contours with using of theory of Raman effect in condensed phase. In spite of the difference of heterogeneous broadening nature for nematics and amorphous phases the proximity of Raman bands widths for these phases is stipulated one of parameters of corresponding averaging statistic distributions. The method of identification and prognostic of structural evolution of phase states for wide class of LC have been proposed.

1. V.Ye. Pogorelov, I.B. Estrela-Llopis, *Mol. Cryst. Liq. Cryst.* **265**, 237 (1995).
2. V.Ye. Pogorelov, I.B. Estrela-Llopis, *J. Mol. Struct.* **348**, 269 (1995).

FA01**30 min 8:30****INFRARED SOURCES FOR SPECTROSCOPY BASED ON DIFFERENCE FREQUENCY GENERATION**

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Rapid advances are being made in infrared sources based on difference frequency generation (DFG) through the introduction of new nonlinear materials, build-up cavity enhancement, and new diode-based pump and signal sources. These infrared sources have obvious application to high resolution molecular spectroscopy. In addition, the combination of all these elements promises a wide variety of compact, rugged, portable IR sources for applications such as environmental monitoring. Recent results obtained for difference frequency mixing in AgGaS₂, periodically poled LiNbO₃, and GaSe using diode, Nd:YAG, and Ti:sapphire pump sources will be reported. The suitability of the sources based on diode and Nd:YAG pumps for atmospheric monitoring has been demonstrated by the detection of ambient methane and CO.

FA02**15 min 9:05****GENERATION AND CONTROL OF SUBMILLIMETER RADIATION WITH LOCKED DBR DIODE LASERS**

HERBERT M. PICKETT, J. C. PEARSON and S. DUBOVITSKY, *Jet Propulsion Laboratory, California Institute of Technology, Mail Stop 183-301, 4800 Oak Grove Dr., Pasadena, CA 91109*.

The ability of low temperature grown GaAs photomixers to radiate the difference frequency of two near infrared lasers has provided an important new means of generating submillimeter radiation^a. A scheme to lock 850 nm DBR diode lasers and generate a precisely known difference frequency in a photomixer is presented as a potential solution to the problems of generation and control of THz frequency radiation. This approach uses two output lasers, a metrology laser and a 10,000 finesse cavity with a 3 GHz free spectral range. The metrology laser and one of the output lasers are locked to different orders of the cavity using electrical feed back based on the Pound, Drever, Hall method^{b,c}. The cavity is temperature stabilized so that the frequency of the metrology laser coincides with a lamb dip in Cs. The second output laser is frequency offset locked to the metrology laser with a synthesizer and a standard phase locked loop. The result is a completely tunable, precisely known difference frequency which can be used to generate THz radiation in the low temperature grown GaAs photomixer.

^aE. R. Brown, K. A. McIntosh, K. B. Nichols and C. L. Dennis, *Appl. Phys. Lett.* **66**, 285 (1995).

^bR. V. Pound, *Rev. Sci. Instrum.* **17**, 490 (1946).

^cR. W. P. Drever, J. L. Hall, F. V. Kowalski, J. Hough, G. M. Ford, A. J. Munley and E. Ward, *Appl. Phys.* **B 31**, 97 (1983).

FA03**15 min 9:22****FAST SCAN BACKWARD WAVE OSCILLATOR SPECTROMETER.**

D. T. PETKIE, T. M. GOYETTE, AND F. C. DE LUCIA

The development of a simple fast scan millimeter and submillimeter wave spectrometer based on a free running Backward Wave Oscillator (BWO), fast and sensitive InSb liquid helium temperature detectors, and a 40 meter long Fabry-Perot (FP) cavity will be presented. In addition to serving as frequency calibration markers, the FP cavity modes also probe the frequency/voltage characteristics of the BWO and the overall characteristics of the system. Nitric acid has served both as a calibrant gas and a sample gas. Typical results from this spectrometer include 100 GHz of spectral data acquired in 5 seconds with the frequency measurement accuracy 50 kHz. The limitations, advantages, and ultimate sensitivity of this spectrometer will be addressed.

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FA04

15 min 9:39

A FEMTOSECOND DEMODULATION SOURCE FOR HIGH-RESOLUTION SUBMILLIMETER SPECTROSCOPY .

T. M. GOYETTE, J. R. DEMERS, W. GUO, K. JUVAN, J. C. SWARTZ, H. O. EVERITT, E. R. BROWN, B. D. GUENTHER, AND F. C. DE LUCIA

A new continuously tunable high resolution millimeter/submillimeter wave (mm/submm) source with a spectral purity better than 10^{-7} has been developed. The source consists of a mode locked Ti:Sapphire laser whose 120fs duration pulses are converted to the mm/submm region by means of a subpicosecond photoconductive switch. The dominant noise source which limits spectral purity can be traced to fluctuations in the argon ion pump laser. An analysis of the spectral purity and system noise will be presented along with sample spectra of OCS transitions at 340GHz and 607GHz.

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Address of Swartz and Juvan: Department of Physics, Duke University, Durham NC 27706.

Address of Brown: Lincoln Laboratory, Massachusetts Institute of Technology, Lexington, MA 02173-9108.

Address of Everitt and Guenther: U. S. Army Research Office, Research Triangle Park, NC 27709.

FA05

15 min 9:56

AN ANALYTIC EXPRESSION FOR THE MOLECULAR EMISSION SIGNAL OBSERVED IN COAXIAL-NOZZLE FOURIER-TRANSFORM MICROWAVE SPECTROSCOPY

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Transient microwave spectroscopy was introduced by Dicke and Romer^{a,b} approximately 40 years ago. In the early eighties, Balle, Flygare, and coauthors developed a time-domain microwave spectrometer based on a pulsed supersonic gas expansion perpendicular to the axis of a Fabry-Perot resonator^c, and provided theoretical expressions for the shape of the observed transient molecular signal^{d,e}. Since the velocity equilibration of the molecules during the gas expansion minimizes Doppler and pressure broadening, the achievable linewidth in such an experiment should be very small. Unfortunately, the short transit time of the polarized gas through the small active region of the cavity limits the resolution. Both sensitivity and resolution of the spectrometer can be greatly improved by a coaxial arrangement of the microwave resonator and the gas expansion source^f. Due to the propagation of the molecular beam along the symmetry axis of the mirrors, both the transit time through the active region of the cavity and the volume of the gas ensemble interacting with the active region of the resonator are maximized. With this arrangement, the lines of the molecular emission signal appear in the frequency domain as completely resolved doublets with individual linewidths of approximately 1kHz (HWHM). The experimental results are explained using the density matrix formalism to yield expressions analogous to the optical Bloch equations. An analytical function for the shape of the free induction decay (FID) of the molecular signal is derived by calculating the transient electrical field using Maxwell's equations.

^aR. H. Dicke and R. H. Romer, Rev. Sci. Instrum. 26, 915(1955).

^bR. H. Dicke and R. H. Romer, Phys. Rev. 99, 532(1955).

^cT. J. Balle and W. H. Flygare, Rev. Sci. Instrum. 52, 33(1981)

^dE. J. Campbell, L. W. Buxton, T. J. Balle, and W. H. Flygare, J. Chem. Phys. 74, 813(1981)

^eE. J. Campbell, L. W. Buxton, T. J. Balle, M. R. Keenan, and W. H. Flygare, J. Chem. Phys. 74, 829(1981)

^fJ.-U. Grabow and W. Stahl, Z. Naturforsch. 45a, 1043(1990)

FA06

30 min 10:30

DIODE LASERS AND NONLINEAR OPTICS FOR SPECTROSCOPY, FROM THE UV TO MILLIMETER WAVES, L. HOLLBERG, J.H. MARQUARDT, S. WALTMAN, and R.W. FOX
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High quality semiconductor lasers that operate at room temperature, in the red and near-IR spectral region, are beginning to play a significant role in spectroscopy.^{a,b} Our group at NIST, is one of many, that are developing and applying diode laser technology to scientific and technical problems. With some modification to the commercial laser devices it is possible to construct compact, efficient, broadly tunable (coarse tuning ~30 nm), single-frequency narrow-linewidth laser systems. Output powers of these tunable lasers range from ~1 to 100 mW with a good spatial beam quality. The spectral coverage of the diode lasers can be extended to the blue, UV, IR and even Far-IR by utilizing the modern techniques of nonlinear optics.^{c,d,e} These methods work very well in some spectral regions and are more challenging in other regions. A good-case example is the use of second harmonic generation in KNbO₃ to produce light near 425 nm, where it is fairly straight forward to produce 10's of milliwatts of usable output power. Access to much of the IR and far-IR can be achieved with difference frequency mixing.^{d,e} Recent advances in the rapidly changing semiconductor laser technology include: commercialization of grating-tuned external cavity lasers, and high power semiconductor amplifiers that can boost output powers to ~500 mW.^f Combining these system with the new nonlinear mixing materials (such as periodically-poled lithium niobate, and GaAs photomixers) opens up a variety of new research opportunities. In addition, many previous applications become more feasible with diode laser sources because the lasers are more efficient, compact and lower cost. The capabilities and limitations of these systems will be illustrated with examples taken from spectroscopic experiments.

^a Diode Laser Spectroscopy, Edit. K. Niemax, special issue of Spectrochimica Acta Reviews, 15, 291, 1993.

^b R.W. Fox, A.S. Zibrov, and L. Hollberg, Semiconductor Diode Lasers, in Methods in Experimental Physics, vol. Atomic, Molecular and Optical Physics, to be published Academic Press (1995).

^c C. Zimmerman, V. Vuletic, A. Hemmerich, and T.W. Hänsch, Appl. Phys. Lett. 66, 2318-2320 (1995). Lew Goldberg and Dahv A. V. Kliner, Opt. Lett., 20, 1145 (1995).

^d U. Simon, Zsolt Benko, M.W. Sigrist, R.F. Curl, and F.K. Tittel, Appl. Opt., 32, 6650-6655 (1993). S. Sanders et al. proceedings of annual meeting of IEEE LEOS '95, 312 (1995).

^e E.R. Brown, F.W. Smith and K.A. McIntosh, J. Appl. Phys. 73, 1480 (1993).

^f J.N. Walpole, E.S. Kintzer, S.R. Chinn, C.A. Wang, and L.J. Missaggia, Appl. Phys. Lett. 61, 740 (1992). D.F. Welch, R. Parke, D. Mehuys, A. Hardy, R. Lang, S. O'Brien, D.S. Scifres, Electron. Lett. 28, 2011-2013 (1992).

FA07

10 min 11:05

NEW LASER LINES AND FREQUENCY MEASUREMENTS OF FULLY DEUTERATED ISOTOPOMERS OF METHANOL

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We report new far-infrared laser lines generated from two fully deuterated isotopomers of methanol: ¹²CD₃OD and ¹³CD₃OD; five from ¹²CD₃OD and 22 from ¹³CD₃OD, which added to the previously reported far-infrared laser lines in these two molecules sums up to 300. The laser lines were mainly pumped by the 10R (regular) and 10SR (sequence) bands of a cw- CO₂ laser. We measured their frequencies, relative intensities, relative polarizations and pump offsets. The laser lines are in the spectral range from 43.697 to 719.426 μm (6 860 664.6 to 416 710.4 MHz).

FA08**10 min 11:17****OPTICALLY PUMPED FAR-INFRARED LASERS FROM METHANOL ISOTOPOMERS:
 $^{12}\text{CD}_3\text{OH}$, $^{12}\text{CH}_3\text{OD}$, AND $^{12}\text{CH}_2\text{DOH}$; NEW LASER LINES AND FREQUENCY
MEASUREMENTS**

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Methanol and ten of its isotopomers have generated over 2000 far-infrared laser lines when pumped by CO_2 lasers. We report here 28 new laser lines from the isotopomers $^{12}\text{CD}_3\text{OH}$, $^{12}\text{CH}_3\text{OD}$, $^{12}\text{CH}_2\text{DOH}$ along with their frequencies, relative intensities, relative polarizations and pump offsets. An efficient CO_2 laser with extended line coverage provided pumping from high J-fundamental, sequence and hot-band CO_2 transitions. Many new short-wavelength (below 100 μm) FIR laser transitions were observed.

FA09**15 min 11:29****RECENT WORK IN HIGH RESOLUTION ROVIBRATIONAL SPECTROSCOPY AT THE
INSTITUTO DE ESTRUCTURA DE LA MATERIA IN MADRID**

Julio Santos, José L. Doménech, Raúl Z. Martínez, Dionisio Bermejo,
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In the past few years, two different laser spectroscopy techniques, Difference Frequency Laser Infrared and Stimulated Raman, have been implemented in our laboratory, and applied to gas phase high resolution studies of rovibrational spectra of small molecules either in bulk, discharge cell or supersonic jet environments. We shall report on the latest results on these experiments.

The Raman technique -instrumental linewidth 70 MHz- has been used to obtain near Doppler-limited spectra of infrared inactive fundamental transitions, and to study energy relaxation in a supersonic jet. It has recently been adapted to the study of higher vibrational levels by using a Raman-Raman double resonance technique. Results on $2\nu_1$ state of CH_4 will be presented. ^a

The Doppler-limited DFIR -instrumental linewidth 3 MHz- has been applied to the study of inert molecules and of the methyl radical generated in an amplitude modulated, hollow cathode discharge cell. Currently, it is being used to study line broadening and shifting at moderate pressures (up to 1 bar). We shall briefly report on lineshifts of rovibrational lines in the overtone CO band, both self-perturbed and perturbed by foreign gases N_2 , O_2 , He and Kr. ^b

^aWork done in cooperation with J.P. Champion and J. C. Hilico from the Université de Bourgogne, Dijon, France.

^bWork done in collaboration with J-P. Bouanich and C. Boulet from the LPMA, Université Paris-Sud, France.

FA10**15 min 11:46****NEW EXPERIENCES WITH THE FOURIER TRANSFORM SPECTROMETER IN THE
MILLIMETER WAVE RANGE**

Antonio Guarnieri, Jens Doose, Nico Nissen, and Heinrich Mäder, *Institut für Physikalische Chemie, Christian-Albrechts-Universität, Olshausenstraße 40-60, D-24098 Kiel, Germany*.

The recently developed "Fourier Transform Millimeter Wave Spectrometer" (FT-MMW) employs a technique of frequency switching which is different from the commonly used amplitude switching method for FT-Spectrometers in the centimeter wave range. Frequency switching is achieved by 180° phase modulation to generate two different sidebands of the master oscillator frequency in the microwave range. Extension of this technique to the millimeter wave range succeeds through frequency multiplication. The application is presently limited to the observation of collision-induced line broadening. Other applications will be possible in the future.

FB01

15 min 8:30

COMPREHENSIVE ANALYSIS OF THE IR SPECTRUM OF Ar-CO, INCLUDING INTERMOLECULAR BENDING AND STRETCHING STATES

YUNJIE XU AND A.R.W. McKELLAR, *Steacie Institute for Molecular Sciences, National Research Council of Canada, Ottawa, Ontario K1A 0R6, Canada.*

The infrared spectrum of the weakly-bound Ar-CO van der Waals complex in the 2150 cm^{-1} region of the CO stretch has been studied using a continuous supersonic slit jet expansion coupled with a tunable laser spectrometer, and also with a cooled (57 K) long-path cell coupled with a Fourier transform spectrometer. Seven new subbands were observed, and numerous previously observed bands were observed in greater detail. Four substates were thus identified for the first time, including the excited van der Waals stretching state, $v_3=1$, and the excited bend, $v_2=1$, within the ground CO stretching state, $v_{\text{CO}}=0$. The observed bending and stretching frequencies were $\nu_2 = 12.014\text{ cm}^{-1}$ and $\nu_3 = 18.110\text{ cm}^{-1}$ (for $v_{\text{CO}}=0$).

A comprehensive simultaneous analysis was made of all the existing infrared and microwave data on the complex for levels with $K < 5$, in order to obtain an accurate and self-consistent set of substate origins, rotational parameters, and centrifugal distortion parameters. A strong Coriolis interaction between $K=1$ of the bend and $K=0$ of the stretch was analyzed in detail. The results are in rather good agreement with energy level calculations by G. Jansen^a which are based on an adjusted *ab initio* potential surface. These calculations also indicate that there is considerable mixing of bending and stretching in Ar-CO, so that, for example, labeling the 12 cm^{-1} vibration as the 'bend' is only very approximate.

^aG. Jansen, *J. Chem. Phys.*, submitted for publication.

FB02

15 min 8:47

SLIT-JET INFRARED SPECTRUM OF THE CO-N₂ COMPLEX

YUNJIE XU AND A.R.W. McKELLAR, *Steacie Institute for Molecular Sciences, National Research Council of Canada, Ottawa, Ontario K1A 0R6, Canada.*

The weakly-bound CO-N₂ complex was studied^a in the $4.7\text{ }\mu\text{m}$ infrared region of the CO stretching vibration using a continuous slit-jet supersonic expansion and a tunable diode laser spectrometer. A total of 152 lines were observed and assigned to four connected subbands with $K = 0\leftarrow 1$, $0\leftarrow 0$, $1\leftarrow 0$, and $2\leftarrow 1$, and to one unconnected subband with $K = 1\leftarrow 1$. Analysis of these bands yielded K -state origins, rotational parameters, and centrifugal distortion parameters. The effective intermolecular separation for the complex in its ground state was found to be $4.025\text{ }\text{\AA}$, and predictions of rotational frequencies were made to aid in the search for CO-N₂ microwave transitions. The spectra observed were surprisingly simple and well-behaved, to the extent that they could virtually be ascribed to a (fictitious) complex of CO with a rare gas atom having a mass of 28 amu. This simplicity may be explained by postulating that the N₂ undergoes relatively free internal rotation in the complex. All but one of the observed bands involve levels which correlate with the rotationless $J = 0$ state of ortho-N₂. Along with a more limited report of the same $K = 1\leftarrow 0$ subband by Kawashima and Nishizawa,^b the present work represents the first spectroscopic observation of this rather basic complex. Further infrared, microwave and theoretical studies should be combined in order to learn more about the orientational structure and intermolecular potential of CO-N₂.

^aY. Xu and A.R.W. McKellar, *J. Chem. Phys.* **104**, 2488 (1996).

^bY. Kawashima and K. Nishizawa, *Chem. Phys. Lett.*, to be published.

FB03

15 min 9:04

INFRARED SPECTROSCOPY OF THE AR-C₂HD COMPLEX: POTENTIAL ENERGY SURFACES

R. J. Bemish and R. E. Miller, *Department of Chemistry, University of North Carolina, Chapel Hill, NC 27599.*

The argon-acetylene complex has been studied by a number of experimental and theoretical groups, with the aim in mind of determining an accurate potential energy surface for this system. Both microwave and infrared spectroscopy have provided detailed rotational and vibrational constants for this system. In addition, scattering experiments have been reported and *abinitio* calculation performed. Even with all of this, there are still some fundamental questions that remain unanswered with regards to the shape of the potential surface. We will review some of this work to outline the current situation. In the present study we have obtained high resolution infrared spectra of the Ar-C₂HD complex with the aim of providing additional molecular constants that could be used to help constrain the potential. Collocation calculations are reported, using a number of potential surfaces, for this and the normal isotopomer. This additional data helps to answer some of these open questions.

FB04

15 min 9:21

Two examples of long lived metastable systems: Ar-HCl ($v=1$) and Ar-DF ($v=1$)

L. Oudejans, B. K. Nauta and R. E. Miller, *Department of Chemistry, University of North Carolina, Chapel Hill, NC 27599.*

High resolution optothermal spectra have been obtained for the Ar-HCl ($v=1$) and Ar-DF ($v=1$) complexes. In both complexes, the vibrational predissociation lifetime is found to be greater than the time of flight of the complexes from the point of excitation by an F-center laser to the bolometer detector. This places a lower limit on the lifetime of 0.6 ms, in analogy to earlier reported Ar-HF ($v=1$) measurements. In addition to this, Stark spectra have been obtained for both complexes to determine the vibrational excited state dipole moments. These will be compared with the theoretical values

FB05

15 min 9:38

Final state distributions upon vibrational predissociation of the HCl dimer

L. Oudejans and R. E. Miller, *Department of Chemistry, University of North Carolina, Chapel Hill, NC 27599.*

Photofragment angular distributions have been obtained for the vibrational predissociation of the HCl dimer. The initial state was selected by exciting the "free"- or "bounded" H-Cl stretch with an F-center laser. Assignment of the final state distributions allows for accurate determination of the dissociation energy of the dimer to be 439(2) cm⁻¹, in good agreement with the recent study of Ni *et al*^a. The influence of the hyperfine interaction on the angular distributions will be discussed.

^aH. Ni, J. M. Serafin and J. J. Valentini *J. Chem. Phys.* **104** 2259 (1996)

FB06

15 min 9:55

Isotopic Substitution of a Hydrogen Bond: A Near-IR Study of All 4 Intermolecular Modes in DF Dimer, Scott Davis, David T. Anderson, and David J. Nesbitt

The near IR combination band spectra of supersonically cooled $(DF)_2$ in the 2900 cm^{-1} to 3300 cm^{-1} region have been recorded with a high resolution slit jet spectrometer. 12 vibration-rotation-tunneling (VRT) bands are observed, representing each of the 4 intermolecular modes ("van der Waals stretch" v_4 , "geared bend" v_5 , "out-of-plane torsion" v_6 , and "anti-geared bend" v_3) built as combination bands on either the v_1 ("free") or v_2 ("bound") DF stretches. Analysis of the rotationally resolved spectra provide spectroscopic constants, intermolecular frequencies, tunneling splittings and predissociation rates as a function both of intra- and inter-molecular excitation. The intermolecular frequencies demonstrate a small but systematic dependence on intramolecular mode, which is exploited to yield frequency predictions relevant to far-IR studies, as well as facilitate direct comparison with full 6-D quantum calculations on trial potential surfaces. Detailed vibrational energy patterns upon H/D isotopic substitution for the *same* potential surface are obtained by comparison with previous combination band studies of all four intermolecular modes in $(HF)_2$. Such analysis reveals, for example, a surprisingly large (25%) and positive shift for the v_4 "van der Waals stretch" upon deuteration. The van der Waals stretch and geared bend degrees of freedom appear to be largely decoupled in $(DF)_2$, in contrast to the strong state mixing previously observed for $(HF)_2$ and indicating the importance of isotopically tuned resonances between bend-stretch intermolecular vibrations. Quantum mechanical analysis of the 4-D eigenfunctions indicate that the isotopic dependence of such a bend-stretch resonance behavior is incorrectly predicted by current hydrogen bond potential surfaces.

Scott Davis: JILA, National Institute of Standards and Technology and Department of Chemistry and Biochemistry, University of Colorado, Boulder, Colorado 80309-0440.

Intermission

FB07

15 min 10:30

Hydrated Proton Clusters

Lars Peder Ojam e, *Department of Quantum Chemistry, Uppsala University*; Sherwin J. Singer, Isaiah Shavitt, *Department of Chemistry, Ohio State University*.

A potential energy surface for $(H_2O)_nH^+$ has been developed based on extensive *ab initio* calculations for $H_5O_2^+$, H_3O^+ , $H_9O_4^+$, and $(H_2O)_2$. It has been tested in simulations of pure water clusters, bulk water, and these same systems containing an excess proton. Features of the potential energy surface are explored in this presentation. An analysis of the radical structural changes that accompany addition of an excess proton to a water cluster is presented. Preliminary results of vibrational calculations in these systems is presented.

FB08**15 min 10:47**HIGH RESOLUTION INFRARED SPECTROSCOPY OF CO₂-N₂O

C. Dutton, A. Sazonov, R.A. Beaudet, Department of Chemistry, University of Southern California, Los Angeles, CA 90089-0482

The absorption spectrum of the weakly bound cluster CO₂-N₂O has been observed by probing the ν_3 asymmetric stretch of CO₂ near 2350 cm⁻¹. Clusters were formed by supersonic expansion of a mixture of N₂O:CO₂ in a 4:1 ratio using He as the carrier gas. Etalon, reference and signal spectra were recorded simultaneously using a transient digitizer and a 386 PC. A nearly planar slipped parallel geometry is observed with the O of NNO nearly over the C of CO₂. R_{cm} and θ are 3.05 Å and 59°, assuming the CO₂ and N₂O are parallel and planar. Both parallel and perpendicular transitions were observed. Approximately 270 lines have been assigned. The ground state rotational constants A, B, and C are 0.294924(12) cm⁻¹, 0.058004(6) cm⁻¹, and 0.048400(6) cm⁻¹, respectively. The quartic centrifugal distortion constants are $D_j = 5.03(17) \times 10^{-7}$ cm⁻¹, $D_{jk} = -3.92(9) \times 10^{-6}$ cm⁻¹, $D_k = 1.26(2) \times 10^{-5}$ cm⁻¹, $\delta_j = 1.61(92) \times 10^{-8}$ cm⁻¹, $\delta_k = 1.77(80) \times 10^{-6}$ cm⁻¹.

FB09**10 min 11:04**AB INITIO CALCULATIONS OF THE CO₂-N₂O VAN DER WAALS COMPLEX

A. Sazonov, R. A. Beaudet, Department of Chemistry, University of Southern California, Los Angeles, CA 90089-0482

Ab initio calculations for CO₂-N₂O equilibrium structures have been done on SCFHF, MP2, and MP4 levels with a 6-311g* basis set. The planar slipped parallel geometry with N₂O oxygen atom close to CO₂ fragment was found to be the most stable one. The molecular parameters, spectroscopic constants, and stabilization energies were compared to the corresponding data on the (CO₂)₂ and (N₂O)₂ van der Waals dimers as well as to the experimental results obtained in the laboratory by high resolution IR spectroscopy in a supersonic expansion. The other features of intermolecular potential for the CO₂-N₂O system will be also discussed.

FB10

15 min 11:16

ROVIBRATIONAL SPECTROSCOPY AND MOLECULAR DYNAMICS OF Ar-HBr

J. HAN, A. L. McINTOSH, Z. WANG, R. R. LUCCESE, AND J. W. BEVAN, *Department of Chemistry, Texas A and M University, College Station, TX 77843.*

High resolution rovibrational spectra of several bands associated with the ν_1 (HBr stretch) of both Ar-H⁷⁹Br and Ar-H⁸¹Br isotopomers have been recorded using a tunable infrared diode laser supersonic jet spectrometer. In addition to the ν_1 fundamental, the combination bands $\nu_1 + 2\nu_2^0$, $\nu_1 + \nu_2^1$, $\nu_1 + \nu_3$, $\nu_1 + 2\nu_2^0 + \nu_3$, the hot band $\nu_1 + 2\nu_2^0 - 2\nu_2^0$, and the difference band $\nu_1 - 2\nu_2^0$ were observed and analyzed. Nuclear quadrupole splittings have been partially resolved in Q branch transitions of the $\nu_1 + \nu_2^1$ band. A strong Coriolis perturbation between the $\nu_1 + \nu_2^e$ and $\nu_1 + \nu_3$ was observed and analyzed. These results have been incorporated to determine an improved H4 intermolecular potential for Ar-HBr. In addition, the intermolecular potential surface for the Ar-HBr with HBr in its $v = 1$ state has also been modeled based on the experimental results of this work.

FB11

15 min 11:33

A ROVIBRATIONAL ANALYSIS OF THE ν_1 AND ν_2 BANDS OF OC-DF BY FTIR SUPERSONIC JET SPECTROSCOPY

J. HAN, A. L. McINTOSH, C. L. HARTZ, AND J. W. BEVAN, *Department of Chemistry, Texas A and M University, College Station, TX 77843.*

We report the application of Fourier transform infrared supersonic-jet spectroscopy to the isotopically enriched weakly bound dimer OC-DF. Using this technique, the ν_1 (DF stretch) and ν_2 (CO stretch) rovibrational bands of this hydrogen bonded complex have been recorded and analyzed. The band origin frequencies, rotational constants, and centrifugal distortion constants of the ν_1 and ν_2 fundamentals have been determined. A Coriolis perturbation between the ν_1 excited state and a dark state was observed around $J' = 13$. Neglecting the influence of other perturbations interacting at higher J' levels, a two-level interaction Hamiltonian was used to predict the band origin and rotational constant of the dark state. The Coriolis interaction constant for this perturbation was determined, within error, by both the deperturbation method and a simple formula which requires only the relative intensities and frequency separation of the doublets observed at the $P(14)$ and $R(12)$ transitions. A lower limit of 1.1 ns was estimated for the vibrational predissociation lifetime of the unperturbed levels in the ν_1 excited state.

FB12

15 min 11:50

VIBRATIONAL OVERTONE (3-0) SPECTROSCOPY OF Ar₂HF AND Ar₃HF

Cheng-Chi Chuang and William Klemperer, *Department of Chemistry, Harvard University, Cambridge, MA 02138*; Huan-Chen Chang, *Institute of Atomic and Molecular Sciences, Academia Sinica, P.O.Box 23-166, Taipei, Taiwan 10764, Republic of China.*

We report laser induced fluorescence spectra for the species Ar₂HF and Ar₃HF. Three bands have been assigned to Ar₂HF. A **b-type** transition band, centered at 11323.80 cm⁻¹ (49 cm⁻¹ red shift) is observed with rotational constants of the upper state A=0.11957, B=0.05855 and C=0.03896 cm⁻¹. This band is consistent with the pure $v=3$ HF stretch of the trimer. A second tenfold weaker **a-type** band with origin at 11387.86 cm⁻¹ is assigned to the in-plane bending combination. A third, even weaker, band with **c-type** rotational structure is observed with origin at 11426.3 cm⁻¹ and is assigned to the out-of-plane bending combination. The in-plane and the out-of-plane bending frequency are 64 cm⁻¹ and 103.5 cm⁻¹ respectively. These vibrations show a quite different dependence upon the HF vibrational state. The pure $v=3$ HF stretch of the tetramer Ar₃HF is observed as a **parallel** band of a symmetric top. The band origin is 11310.45 cm⁻¹ (62 cm⁻¹ red shift); the upper state rotational constant B=0.03975 cm⁻¹. All of the spectra lines shows a Doppler shape, with no evidence for vibrational predissociation. The width of the lines of all of the species Ar_nHF, n=0-3, are well fitted by a single temperature.

FC01

15 min 8:30

COORDINATES, HAMILTONIAN AND SYMMETRY OPERATIONS FOR THE SMALL-AMPLITUDE VIBRATIONAL PROBLEM IN INTERNAL-ROTOR MOLECULES LIKE CH_3CHO , JON T. HOUGEN, Molecular Physics Division, National Institute of Standards and Technology, Gaithersburg, MD 20899.

The small-amplitude vibrational problem in molecules with a periodic large-amplitude vibration exhibits some features not found in the traditional vibration-rotation formalism¹. Motivated by the long-term goal of trying to understand the mechanism(s) by which internal rotation of methyl tops strongly enhances intramolecular vibrational energy redistribution, we have constructed a vibration-torsion-rotation Hamiltonian for molecules containing one C_{3v} rotor, which has many analogies with that for quasi-linear molecules. In this formalism, internal rotation motion is taken to be slow compared to all other vibrational motions, so that (i) the small-amplitude vibrational problem is solved for each value of the torsional angle (in the spirit of the Born-Oppenheimer approximation), and (ii) the angular momentum operator associated with internal rotation motion is grouped with the three components of the total angular momentum operator rather than with the vibrational linear momentum operators.

One surprising group-theoretical result has emerged. Even though the molecular symmetry group for basis set functions in the principal axis system (or rho axis system) is isomorphic with C_{3v} , small-amplitude vibrational eigenvectors resulting from diagonalization of the GF matrix do not necessarily belong to irreducible representations of C_{3v} , but may in fact change sign when the methyl top is rotated by 2π . As a result, a double group of C_{3v} must be used to classify these eigenvectors. This sign change in vibrational wavefunctions under one torsional revolution, which is reminiscent of the sign change in electronic wavefunctions under one vibrational "revolution" when a Jahn-Teller effect is present², seems to be related to the fact that the CH_3CHO molecule passes through two chemically different C_s configurations (staggered and eclipsed with respect to the aldehyde H) during the internal rotation motion.

The usefulness of the present theoretical formalism has not yet been determined, and a number of questions concerning its application still remain. Further work is thus planned, in which this formalism will be tested by using it to study various torsionally mediated perturbations in methanol and acetaldehyde.

¹E. B. Wilson, Jr., J. C. Decius and P. C. Cross, "Molecular Vibrations," McGraw-Hill, New York, 1955.

²H. C. Longuet-Higgins, *Advances in Spectroscopy* 2, 429-472 (1961).

FC02

15 min 8:47

METHYL ROTOR INTRAMOLECULAR DYNAMICS OF GASEOUS NITROMETHANES NO_2CH_3 AND $\text{NO}_2\text{CH}_2\text{D}$

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The internal rotation of the methyl group in nitromethanes NO_2CH_3 and $\text{NO}_2\text{CH}_2\text{D}$ are studied through the CH bond stretching overtones ($\Delta v = 1$ to 6). The spectra of the gaseous compounds are recorded by FTIR ($\Delta v = 1$ to 4) and by intracavity dye laser photoacoustic spectrometry ($\Delta v = 5$ and 6) at low resolution (0.5 to 2 cm^{-1}).

A quantum theory, assuming an anharmonic coupling of the $\nu(\text{CH})$ mode with the methyl group internal rotation is used to analyse the experimental data (1). The used conformational dependent parameters are provided by ab-initio calculations (1,2). Theoretical calculations based on this model show that the effective internal motion potential in the high excited CH stretching states is essentially due to the vibrational energy contribution.

The Fermi resonance couplings with the combination states involving C-H stretch / CH_3 or CH_2D bending modes and C-H / C-D stretch modes are also considered and modelled. Contrary to what is observed in cyclopentene (3), these phenomena lead only to weak redistribution of the energy localized at the $\Delta v = 3$ vibrational state. At high vibrational energy ($\Delta v = 4$ to 6), the major part of the features of the $\nu(\text{CH})$ overtone spectra are determined by both methyl group internal rotation and vibration-rotation structure. The central band can be related to the average CH stretch during the methyl group rotation whereas the lower frequency peak can be assigned to the CH stretch of a C-H bond in a plane perpendicular to the molecular plane and the higher frequency one to the CH stretch of a C-H bond in the molecular plane.

At low vibrational energy ($\Delta v = 1$ and 2), the Coriolis coupling between the internal rotation and the two perpendicular stretching normal modes $\nu_a(\text{CH}_3)$ and $\nu_s'(\text{CH}_3)$ is also modelled.

1. D. Cavagnat, L. Lespade and C. Lapouge, *J. Chem. Phys.* 103, 10502 (1995).

2. D. Gorse, D. Cavagnat, M. Pesquer and C. Lapouge, *J. Phys. Chem.*, 97, 4262 (1993).

3. S. Rodin-Bercion, D. Cavagnat, L. Lespade and P. Maraval, *J. Phys. Chem.*, 99, 3005 (1995).

FC03

15 min 9:04

METHYLAMINE TORSIONAL-WAGGING FIR SPECTRUM HNH BENDING ANGLE DEPENDENCE. Y. G. SMEYERS, M. VILLA and M.L. SENENT.

The methylamine potential energy function for the torsion and wagging vibration motions depend upon the HNH bending angle of the amine group (1). By using the RHF/MP2 approximation and a 6-31G++(3df, 3pd) basis set the energy potential surface and the kinetic parameters are calculated by considering the HNH angle a constant and considering it as a variable. With the former results the experimental inversion barrier (2) reported in the literature can be properly reproduced. With a suitable symmetry adapted potential function the torsional-wagging energy levels are calculated, and compared with available experimental data (3). The former work introduces the HNH bending angle as a third variable in the torsional-wagging FIR spectrum and is an initial step in considering the methylamine as a three dimensional non-rigid molecule.

1) Ab-initio determination of the torsional and wagging FIR spectrum of methylamine. Y.G. Smeyers, M. Villa and M.L. Senent.

2) M. Kreglewski and F. Winther, J. Mol. Spectrosc., 156, 261 (1992).

3) M. Kreglewski, in Structure and Conformations of Non-Rigid Molecules, (Eds. J. Laane et al.), NATO-ASI S., Kluwer Ac., Dordrecht, 1993, pp. 29-43.

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Address of M. Villa: Departamento de Quimica, U.A.M.-I, Av. La Purisima y Michoacan, CP 09340, Mexico D.F., MEXICO.

FC04

15 min 9:21

THEORETICAL STUDY OF VIBRATIONAL OVERTONE SPECTROSCOPY AND DYNAMICS IN METHANOL, L.O. HALONEN AND K.K. LEHMANN, Department of Chemistry, Princeton University, NJ 08544

Experimentally observed coupling^a between OH and CH stretching modes in the high overtone region has been modelled successfully in terms of a curvilinear internal coordinate Hamiltonian including harmonic coupling between anharmonic OH and CH stretching oscillators and cubic Fermi resonance kinetic and potential energy couplings between CH stretches and HCH bends. The Hamiltonian matrices have been setup in block diagonal forms including only resonant states. The potential energy parameters have been optimised by the least squares method using experimental vibrational term values as data. The OH/CH stretch interaction parameter obtained agrees well with the one calculated by perturbation theory from a published *ab initio* harmonic force field. The model has reproduced well experimental band origins in the OH stretching overtone region and it has provided assignments for the bending overtones in the CH stretching fundamental region. Finally, a unitary transformation is found from the internal coordinate representation to the corresponding normal coordinate representation providing a set of normal coordinate parameters like diagonal anharmonicity parameters, Darling-Dennison resonance constants and cubic Fermi resonance force constants. Our results confirm the experimental finding of energy redistribution between the OH and CH stretching modes on 100 fs time scale at 5ν_{OH}.

^aL. Lubich, O. V. Boyarkin, R.D.F. Settle, D.S. Perry, and T.R. Rizzo, Faraday Discuss. Chem. Soc. (in press).

FC05

15 min 9:38

THE PERPENDICULAR C-H STRETCHING BAND ν_9/ν_{13} AND THE TORSIONAL POTENTIAL OF DIMETHYLACETYLENE. J. PLÍVA, Department of Physics, Pennsylvania State University, University Park, PA 16802, A.S. PINE, NIST, Gaithersburg, MD 20899, and S. ČIVIŠ, J. Heyrovský Institute of Physical Chemistry, Czech Academy of Sciences, 18223 Prague, Czech Republic.

The perpendicular band of the fourfold degenerate C-H stretching vibration of dimethylacetylene (2-butyne) has been measured in the region 2955 - 3065 cm^{-1} with Doppler-limited resolution at ~ 195 K on a difference-frequency laser spectrometer, and on a high resolution Fourier transform instrument at ~ 295 K as well as in a molecular jet at ~ 20 K. Over 700 P-and R-branch lines from 37 different subbands of this band, plus 25 additional unresolved Q-branches were assigned and fitted to the model of rotational-torsional interactions described by Bunker and di Lauro to determine spectroscopic constants for the upper C-H stretching state and for the Fourier components of the torsional potential in the ground and excited states. The results yield the value $6.316 \pm 0.034 \text{ cm}^{-1}$ for the barrier to internal rotation in the ground state, and $6.643 \pm 0.006 \text{ cm}^{-1}$ for the C-H stretching state. This value for the ground state barrier is somewhat higher than that recently determined from an analysis of the CH_3 -rocking band by Bunker et al.

FC06

15 min 9:55

AN ADIABATIC MODEL OF THE BENDING DYNAMICS OF ACETYLENE

ANNE B. McCOY, Department of Chemistry, The Ohio State University, Columbus, OH 43210.

The dynamics and spectroscopy of ($J = 0$) acetylene bending degrees of freedom are investigated using a reduced dimensional Hamiltonian, derived using an adiabatic separation of slow bending motions from fast stretching motions.^a The seven adjustable parameters in this model are the force constants of a restricted sextic expansion of an effective potential, which have been fit to five experimentally determined transition energies and the two harmonic frequencies. We find that the eigenvalues of this model Hamiltonian reproduce the observed transition energies for states with up to 10 600 cm^{-1} of vibrational excitation. A dispersed fluorescence spectrum out of the excited \tilde{A} state, calculated from this model, will be compared to the experimental spectrum obtained by Solina, *et al.*^b Pathways for energy flow out of the experimental zero-order bright state will also be discussed. With minor modification, a global bend force field is determined that qualitatively describes the vinylidene vibrations and quantitatively describes the acetylene vibrations, allowing for extensions of this effective force field to the development of a global potential for acetylene.

^aA. B. McCoy and E. L. Sibert, *J. Chem. Phys.*, submitted

^bS. A. Solina, J. P. O'Brien, R. W. Field and W. F. Polik, *Ber Bunsenges. Phys. Chem.*, **99**, 555 (1995).

FC07

15 min 10:30

THEORY OF ODD TORSIONAL TRANSITIONS IN THE $V - N$ RESONANCE RAMAN SPECTRUM OF ETHYLENE

J. K. G. WATSON, W. SIEBRAND, M. Z. ZGIERSKI, *Steacie Institute for Molecular Sciences, National Research Council of Canada, Ottawa, Ontario, Canada K1A 0R6*; M. PAWLIKOWSKI, *Department of Computational Methods in Chemistry, Jagiellonian University, 30-060 Cracow, Poland*.

The $V - N$ resonance Raman spectrum of ethylene^a shows a long progression in even quanta of the ground-state torsional mode $\nu_4''(a_u)$. Bands approximately midway between the even quanta have been assigned^b to transitions to odd quanta of ν_4'' . Such transitions are forbidden according to the usual $g \nleftrightarrow u$ selection rule of Raman spectroscopy. Here we consider the theory of the intensity of such transitions allowing for the fact that the excited state is twisted by 90° at equilibrium, using Hougen's double group theory^c. From approximate one-dimensional torsional potentials of the V and N electronic states, it is shown that good qualitative agreement between observed and calculated intensities is obtained. The electronic transition moment is assumed to be proportional to $\cos \theta$, where θ is the torsional angle, but the calculated relative intensities are not sensitive to the precise torsional dependence. More detailed theory will require consideration of the avoided crossing affecting the V state^d.

^aR. J. Sension and B. S. Hudson, *J. Chem. Phys.* 90, 1377 (1989).

^bW. Siebrand and M. Z. Zgierski, *J. Raman Spectrosc.* 21, 263 (1990).

^cA. J. Merer and J. K. G. Watson, *J. Mol. Spectrosc.* 47, 499 (1973).

^dC. Petrongolo, R. J. Buenker, and S. D. Peyerimhoff, *J. Chem. Phys.* 76, 3655 (1982).

FC08

15 min 10:47

PENDULAR STATES AND IVR

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There has been long-term interest in developing methods to align or orient molecules to study steric effects in collisions. Recently, Friedrich and Herschbach and Loesch and Remscheid have explored the use of large static electric fields to "brute-force" orient linear molecules. For molecules excited to regions of high vibrational state density where intramolecular vibrational energy redistribution (IVR) occurs, additional complications need to be considered when designing experiments which require that the excited molecules be aligned or oriented. We have recently shown, for example that a molecule excited to a single molecular eigenstate in regions of high state density is no longer deflected by inhomogeneous fields when the mean spacing between vibrational levels is on the order of the mean molecule-field interaction strength. The present talk explores theoretically the consequence of using "brute force" orientation techniques for molecules excited to regions where IVR is important. The molecule HCCF is chosen as a model system for this study since the anharmonic force field is well characterized, allowing a realistic description of the energy levels and couplings in the high-density-of-states regime. Our results show rapid dephasing of the orientation, even in the absence of any explicit Coriolis coupling of the vibration and rotational degrees of freedom. We find that the effect is induced by nonadiabatic couplings of the pendular ladders built upon different vibrational states. The nonadiabatic couplings require that the rotational constants or dipole moments differ between vibrational states in order that the pendular wavefunctions be nonorthogonal. The present results suggest that the orientation lifetime will be similar to the IVR lifetime when the "brute-force" approach is used to orient molecules in regions of high vibrational state density.

THE CLASSICAL DYNAMICS OF MOLECULES WITH FERMİ RESONANCE

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Due to the 1:2 Fermi resonance, the vibrational levels of molecules like CS₂ or CO₂ cannot be obtained by a simple Dunham expansion, but require instead the diagonalisation of an Hamiltonian matrix:

$$\langle v_1, v_2 | H | v_1, v_2 \rangle = \sum w_i (v_i + d_i / 2) + \sum x_{ij} (v_i + d_i / 2) (v_j + d_j / 2) + \dots$$

$$\langle v_1, v_2 | H | v_1 - 1, v_2 + 2 \rangle = -k v_1^{1/2} (v_2 + 1) + \dots$$

The dynamics of the classical counterpart of this Hamiltonian has been studied recently, leading to analytical expressions for the action integrals and classical frequencies, as well as to an exhaustive description of the geometry of the phase space (1,2). These results have been applied to three problems of interest. First, the observed vibrational levels of CS₂ up to 10000 cm⁻¹ energy have been assigned by replacing the good quantum number, which is destroyed by the Fermi resonance, by the remaining semiclassical quantum number obtained from Einstein-Brillouin-Keller (EBK) quantization conditions (3). In addition, EBK quantization enables one to describe the anticrossing of quantum levels as arising classically from the dynamical tunnelling between quantizing tori (4). Also, the first 44 levels arising from combinations and overtones of the stretching and bending vibrations of CS₂ were reproduced up to 5000 cm⁻¹ vibrational energy using Berry and Tabor's Trace Formula (5).

(1) M. Joyeux, Chem. Phys. 185, 263 (1994)

(4) M. Joyeux, J. Chem. Phys. 102, 2816 (1995)

(2) M. Joyeux, Chem. Phys., in press

(5) M. Joyeux, Chem. Phys. Letters 247, 454 (1995)

(3) M. Joyeux, J. Mol. Spectry, in press

NATURE OF BARRIER FORCES IN ACETALDEHYDE,

D. GUO and L. GOODMAN, Wright and Rieman Chemistry Laboratories,
Rutgers University, New Brunswick, New Jersey 08903

Natural bond orbital analysis of the internal rotation barrier in ground state acetaldehyde carried out using HF 6-31G(d,p) wavefunctions shows that the largest barrier forming energy terms are weakening of the C-C (σ) and methyl C-H out-of-plane bonds. The analysis rationalizes the weakening of the former (the largest single barrier forming energy term) to be antibonding character introduced into the C-C bond by charge transfer involving bonding and antibonding C_{me}-H_{ip} and adjacent C-H_{ald} orbitals. Weakening of the C_{me}-H_{op} bond is more complicated; e.g., involving antibonding character obtained by charge transfer from both σ and π -hyperconjugative orbitals. Pauli exchange repulsions are calculated to be unimportant sources of the barrier.

FC11

15 min 11:38

WHERE DOES THE DIMETHYL ETHER INTERNAL ROTATION BARRIER COME FROM?

V. POPHRISTIC, L. GOODMAN, *Wright and Rieman Chemistry*

Laboratories, Rutgers University, New Brunswick, NJ 08903

The barrier to methyl internal rotation in dimethyl ether is analyzed through decomposition of the barrier energy by symmetry partitioning and natural bond orbital analysis.

The largest single contribution to the barrier is the energy change of the oxygen σ lone pair orbital, largely due to the rehybridization at the top-of-barrier (staggered) conformation. The main structural change, leading to the decrease in s and increase in p character of this orbital, is the opening of the COC angle, occurring because of the increased Pauli exchange repulsion between C-H(in plane) orbitals. This interaction is among the major barrier forming terms, but is far less important than the change in the energy of the lone pair σ orbital on oxygen. Charge transfer energy contributions are also important, but through the contribution of many small barrier forming terms.

This work was supported by National Science Foundation, Petroleum Research Fund and through a grant of C-90 computer time from Pittsburgh Supercomputer Center.

FC12

15 min 11:55

FERMI RESONANCES AND LOCAL MODES IN XH_3 TYPE PYRAMIDAL AND IN XH_4 TYPE TETRAHEDRAL MOLECULES, **L.O. HALONEN**, Department of Chemistry, Princeton University, NJ 08544

Curvilinear internal coordinate Hamiltonians are used to include all vibrational degrees of freedom in XH_3 and XH_4 type molecules like AsH_3 and CH_4 . Approximate but in practice accurate kinetic energy operators are obtained by expanding kinetic energies as Taylor series around equilibrium configurations. In XH_3 the bending vibrations are treated as coupled valence angle oscillators. In XH_4 , due to the redundancy condition between valence angle coordinates, symmetrized internal coordinates are used for the bending vibrations. Hamiltonian matrices are setup in block diagonal forms by including only states which are in resonance with each other by Fermi resonance or by local mode coupling terms. Least squares methods with experimental vibrational band origin data are used to determine potential energy surface parameters. Good agreements are obtained with published surfaces calculated by *ab initio* methods. Unitary transformations from the internal coordinate formulations to equivalent normal coordinate representations are shown to provide simple relations between many customary vibrational parameters.

FC13

10 min 12:12

Theoretical study of avoided resonance overlapping and trapping effect in predissociation processes.

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The interaction of overlapping resonances and the resulting segregation between trapped and short-lived decay modes are studied in model cases of vibrational and electronic predissociations. Departure from the energy independent effective Hamiltonian formalism is shown to be decisive for a proper description of the migration of the resonance energies and widths when the strength of the external coupling is increased. Three different methods are used in a complementary way for analyzing this behaviour: the energy dependent partitioning method, the complex scaling method and the wavepacket propagation technique. The transition from the diabatic to the adiabatic regime is discussed in the electronic predissociation case.

FC14

10 min 12:24

Ab initio calculation of the photoabsorption cross section of NO₂ by the two-dimensional reflection method.

A. DELON, B. KIRMSE, R. JOST, *LCMI/CNRS BP166, 38042 Grenoble Cedex 9, France*; J. Liévin, *Laboratoire de Chimie Physique Moléculaire, Université Libre de Bruxelles, CPI 160/09, B-1050 Bruxelles, BELGIUM*.

The C_{2v} potential energy surfaces of the X^2A_1 , A^2B_2 and B^2B_1 states of NO₂ are calculated at a high level of theory (CASSCF/CMRCI/cc-pVTZ), together with the corresponding dipole moment surfaces for the transitions $X-A$ and $X-B$. All surfaces are fitted to a quadratic polynomial form in the symmetric stretching and bending coordinates, around the equilibrium geometry of the ground state. These *ab initio* data are used to calculate the relative and absolute photoabsorption cross sections by applying the two-dimensional reflection method^a, modified for taking the quadratic form of the potential energy surfaces into account. The theoretical cross section is found in good agreement with the experimental spectrum. The sensitivity of the calculated cross section with the level of *ab initio* theory will be discussed.

^asee R. Schinke, "Photodissociation dynamics", Cambridge University Press (1993).

FD01

15 min 8:30

MAGNETIC FIELD TUNING OF THE NO₂ PHOTODISSOCIATION THRESHOLD

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The lowest photodissociation threshold of NO₂, located at $25128.57 \pm 0.05 \text{ cm}^{-1}$, is now well characterized: below the threshold, the highly excited vibronic levels of NO₂, observed by LIF in a jet, have a lifetime of a few μsec ; above the threshold, the resonant levels have a lifetime shorter than 10^2 psec and no fluorescence can be observed, because the molecule dissociates. The products, NO and O, are formed in their ground states: $\text{NO}_2(X^2A_1) + h\nu \rightarrow \text{NO}(^2\Pi_{1/2}) + \text{O}(^3P_2)$. We have studied by LIF the effect of a magnetic field on the dissociation threshold. The energy of the ground state of NO₂ ($N=0, K=0, J=1/2$) is lowered by $-\mu_B B$ for the $M_S=1/2$ component. The energy of the NO is unaffected ($g \approx 0$ for the $^2\Pi_{1/2}$ state), while the energy of the oxygen atom is splitted into 5 components ($J=2$). The lowest component, $M_J=-2$, which correspond to the energetic threshold, is lowered by $-3\mu_B B$, because the 3P_2 state has a Landé factor of $3/2$. Consequently, we predict that the energy of the photodissociation threshold is lowered by $-2\mu_B B$. We have experimentally and quantitatively observed this effect: the photodissociation threshold observed by LIF is lowered by 13.2 cm^{-1} in a magnetic field of 14 Tesla! The fact that we have to consider only the energy of the upper levels (and not their quantum numbers) is a consequence of the strong mixing (chaos) within the rovibronic levels of NO₂ near the dissociation energy^a.

^aR.Georges, A.Delon and R.Jost, *J.Chem.Phys.* **103**, 1732 (1995). A.Delon, R.Georges and R.Jost, *J.Chem.Phys.* **103**, 7740 (1995).

FD02

15 min 8:47

PREDISSOCIATION OF RYDBERG STATES OF CO INVESTIGATED BY THE DETECTION OF C(³P_J) FRAGMENT

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Carbon atom generation following the predissociation of Rydberg states of CO has been investigated ^a. The Rydberg states of CO were prepared by two-color double resonant excitation through the $3s\sigma B^1\Sigma^+$ state and the atomic carbon fragment was detected by resonance-enhanced multiphoton ionization. The $4s \sim 6s$ ($v = 0$), $5s$ ($v = 1$), $4p \sim 5p$ ($v = 0$), $3d\pi$ ($v = 0, 1$), $4d\sigma$ ($v = 0$), $5d\sigma$ ($v = 0$), $4f \sim 5f$ ($v = 0$) Rydberg states and the $W^1\Pi(v = 2, 3)$ state were found to generate 3P carbon atom.

Mechanism of the predissociation of these high Rydberg states will be discussed based on the atomic carbon fragment yield measurement and on Doppler line shape measurement.

^aT. Ebata, T. Sutani, and N. Mikami, *Chem. Phys. Lett.* **240**, 357 (1995).

FD03

15 min 9:04

PHOTOIONIZATION SPECTROSCOPY OF THE MIXED METAL DIMER MgLi, K.R. BERRY AND M.A. DUNCAN, Department of Chemistry, University of Georgia, Athens, GA 30602.

An electronic spectrum is observed for the new heteronuclear metal dimer, MgLi. This dimer is produced by laser vaporization of a Mg rod that is coated with a thin, vacuum deposited Li layer in a pulsed nozzle cluster source. Resonant Two-Photon Ionization (R2PI) is used to collect the spectra for the $^{24}\text{Mg}^7\text{Li}$, $^{25}\text{Mg}^7\text{Li}$, and $^{26}\text{Mg}^7\text{Li}$ isotopomers. One short band system is observed around 320 nm. Preliminary analysis of this excited state yields the following spectroscopic constants:

$$\omega_e' = 260 \text{ cm}^{-1}, \omega_e x_e' = 4 \text{ cm}^{-1}.$$

FD04

15 min 9:21

PHOTODISSOCIATION SPECTROSCOPY OF $\text{Ca}^+(\text{H}_2\text{O})$ AND $\text{Ca}^+(\text{D}_2\text{O})$, C. T. SCURLOCK, S. H. PULLINS, J. E. REDDIE AND M. A. DUNCAN, Department of Chemistry, University of Georgia, Athens, GA 30602.

Electronic spectra are observed for the mono-solvated metal cation complexes $\text{Ca}^+\text{-H}_2\text{O}$ and $\text{Ca}^+\text{-D}_2\text{O}$ using Resonance Enhanced Photodissociation Spectroscopy. The clusters are produced in a laser vaporization/supersonic expansion source and the mass-analyzed product ion is observed using a time-of-flight mass spectrometer. Both Ca^+ and CaOH^+ (or CaOD^+) dissociation products are observed on sharp resonances. The observed features are assigned to the $(2)^2\text{B}_2\text{-X}^2\text{A}_1$ and $(2)^2\text{B}_1\text{-X}^2\text{A}_1$ transitions, with vibrational progressions in the Ca-OH_2 stretching mode. Spectroscopic constants are $\text{Ca}^+\text{-H}_2\text{O}$: $(2)^2\text{B}_2\text{-X}^2\text{A}_1$ ($T_0 = 21,464 \text{ cm}^{-1}$, $\Delta G_{1/2} = 357.9 \text{ cm}^{-1}$) and $(2)^2\text{B}_1\text{-X}^2\text{A}_1$ ($T_0 = 22,273 \text{ cm}^{-1}$, $\Delta G_{1/2} = 335.9 \text{ cm}^{-1}$); and $\text{Ca}^+\text{-D}_2\text{O}$: $(2)^2\text{B}_2\text{-X}^2\text{A}_1$ ($T_0 = 21,447 \text{ cm}^{-1}$, $\Delta G_{1/2} = 350.9 \text{ cm}^{-1}$) and $(2)^2\text{B}_1\text{-X}^2\text{A}_1$ ($T_0 = 22,261 \text{ cm}^{-1}$, $\Delta G_{1/2} = 324.1 \text{ cm}^{-1}$). These transitions are rotationally resolved about the a -principal axis, and confirm the structure of the complex to possess C_{2v} symmetry. In addition the $\text{Ca}^+\text{-OH}_2$ bond distance is determined to be 2.22 \AA and the H-O-H bond angle 106.8° in the ground state.

FD05

15 min 9:38

Photofragment Spectroscopy of HI Photodissociation.
1. Doppler Spectroscopy of the Hydrogen Fragment

Denis J. Gendron, John W. Hepburn,
CMBLC, Dept. of Chemistry, University of Waterloo, Ontario, CANADA.

The photodissociation of HI has been investigated at various photolysis wavelengths in the first continuum. The dynamic of the process was probed by Doppler spectroscopy at the Lyman α transition of the H atom products. The β -parameters and the branching ratio of the two product channels have been measured at 8 photolysis wavelengths across the first continuum of HI.

FD06

10 min 9:55

VIBRATIONALLY MEDIATED PHOTODISSOCIATION OF HCN

C. R. Bucher, B. M. Harvey AND K. K. Lehmann, *Department of Chemistry, Princeton University, Princeton N. J. 08544.*

Recently, the dissociation mechanism of HCN by vibrationally mediated photodissociation has been examined. Exciting the C-H stretch with four quanta and photodissociating the molecule with 220 nm light generates CN in the first excited electronic $\tilde{\text{A}}^2\Pi$ state rather than the ground $\tilde{\text{X}}^2\Sigma^+$ state. The CN fragment is detected by probing the $\tilde{\text{B}}^2\Sigma^+ \leftarrow \tilde{\text{A}}^2\Pi$ (1-0) band and monitoring the laser induced fluorescence (LIF) via the $\tilde{\text{B}}^2\Sigma^+ \rightarrow \tilde{\text{X}}^2\Sigma^+$ (1-1) transition. Progress on the analysis of the LIF spectrum and the nascent product distribution will be presented.

Intermission

FD07**10 min 10:30****Concerted Reaction on the Timescale of Molecular Vibrations**Una Marvet, Marcos Dantus, *Department of Chemistry, Michigan State University, East Lansing, MI.*

High energy excitation of gem-dihaloalkanes produces molecular iodine as one of the products. Femtosecond transition state spectroscopy (FTS) of this reaction reveals coherent vibrational dynamics in the iodine fragment. Fourier analysis of the transient reveals a bimodal distribution of vibrational levels in the D' state of iodine, consistent with the observed dynamics. A reaction pathway is proposed to explain the observed energy distribution.

FD08**15 min 10:42****Femtosecond Photoassociation Spectroscopy (FPAS)**Una Marvet, Marcos Dantus, *Department of Chemistry, Michigan State University, East Lansing, MI.*

The method femtosecond photoassociation spectroscopy (FPAS) is applied to the association of gas-phase mercury atoms to form dimers in the D1u state. Coherent bond formation is demonstrated by rotational anisotropy in the product.

FD09**15 min 10:59****REACTION OF NFCl₂ WITH ARGON METASTABLES**YEYGENIYA I. GERHANOVICH, JULANNA G. GILBERT, *Department of Chemistry, University of Denver, Denver, CO 80208.*

The reaction of NFCl₂ with metastable argon atoms was investigated. When NFCl₂ was admitted to a stream of argon metastables (³P₂), visible and UV emission was observed. Two sources of the visible emission were identified. A sharp peak at 528 nm was assigned to the Δv=0 sequence band of the b¹Σ⁺-X³Σ⁻ transition in NF, and a peak at 664 nm was assigned to the Δv=0 sequence band of the b¹Σ⁺-X³Σ⁻ transition in NCl. The Δv= -1, +1, +2, and +3 sequence bands of the NCl b-X transition were also observed with up to v=12 levels populated. The vibrational excitation in the NF and NCl fragments has implications for the geometry of the excited state of NFCl₂ formed in the Ar(³P₂)+NFCl₂ reaction. The UV emission spectrum consisted of two bands with maxima at 256 nm and 198 nm. The intensity distribution of the UV emission was identical to the emission that was observed when Cl₂ was added to the stream of argon metastables and was assigned to electronically excited Cl₂ formed via Cl₂ + Ar(³P₂). The source of the Cl₂ is either Cl₂ contamination in the NFCl₂ sample, or Cl₂ formed during the reaction of NFCl₂ with Ar(³P₂). To examine the energetics of the NFCl₂+Ar(³P₂) reaction, G1 and G2 methods were used to calculate the ΔH_{form} of NFCl₂.

FD10

10 min 11:16

Ab initio CALCULATIONS ON THE PHOTOLYSIS OF CHLORINE NITRATE (ClONO_2), L.-Y. CHOW CHIU, Department of Chemistry, Howard University, Washington DC 20059; M. H. LIN,^a Department of Chemistry, The Catholic University of America, Washington DC 20064 and S. T. LAI, Vitreous State Laboratory, The Catholic University of America, Washington DC 20064

Chlorine Nitrate (ClONO_2), which serves as a temporary reservoir in the stratosphere¹ for both NO_x (i.e. NO and NO_2) and ClO_x (i.e. Cl and ClO) species, may have three different UV photolysis pathways: (1) $\text{ClONO}_2 \rightarrow \text{Cl} + \text{NO}_3$, (2) $\text{ClONO}_2 \rightarrow \text{ClO} + \text{NO}_2$ and (3) $\text{ClONO}_2 \rightarrow \text{O} + \text{ClONO}$. We have analyzed the first path way. Geometries and energies of the initial state ClONO_2 (1^1A), the final states NO_3 (2^1A) + Cl ($2P$) and the transition state $\text{Cl}\cdots\text{ONO}_2$ have been optimized by using $\text{HF}/6\text{-}31\text{G}^*$ basis set of the GAMESS program. The results obtained for the initial state agrees with that of Grana et al.² The energy of the transition state is 0.1058 h above the initial state and 0.0807 h above the final state.

a) Now at Department of Chemistry, Xiamen University, Xiamen 361005, China

1. R. Zander, C.P. Rinsland, C.B. Farmer, L.R. Brown, and R.H. Norton, *Geophys. Res. Lett.* **13**, 757 (1986).

2. A. M. Grana, T. J. Lee, and M. Head-Gordon, *J. Phys. Chem.*, **99**, 3493 (1995).

FD11

15 min 11:28

THE EFFECTS OF TRIPLET PERTURBERS ON PHOTOPHYSICAL PROCESSES IN ACETYLENE

Stephen Drucker, Jonathan P. O'Brien, Paresh Patel, and Robert W. Field, *MIT*, 77 Massachusetts Avenue, Cambridge, MA 02139.

We have recorded excitation spectra of the acetylene $\tilde{A}^1A_u \leftarrow \tilde{X}^1\Sigma_g^+$ transition by measuring simultaneously the total emission in two spectral regions: UV (200-400 nm) and NIR (0.9-1.5 μm). UV emission is due to well-characterized¹ $\tilde{A} \rightarrow \tilde{X}$ transitions. The source of the NIR signal is suggested by the emission patterns within the subbands studied, $V_0^2K_0^1$ and $V_0^3K_0^1$. (V denotes the *trans*-bending mode.) The NIR:UV intensity ratio is approximately constant throughout the $V_0^2K_0^1$ subband. This is consistent with excited C_2H or C_2 as the carrier of the NIR signal, because these species, capable of emitting in the NIR^{2,3}, could be produced *via* multiphoton processes² resonantly enhanced by the \tilde{A} state as intermediate. The $V_0^3K_0^1$ subband shows significantly more fluctuation in the NIR:UV intensity ratio than does the $V_0^2K_0^1$ subband. The one-quantum increase in *trans*-bending excitation enables accidental resonances with background states to modulate the NIR emission pattern. Triplet perturbers could participate in this process by modifying the resonance enhancement of C_2H or C_2 production. Mixed S_1 -triplet states could additionally contribute to the NIR signal through $T_n \rightarrow T_1$ ($n > 1$) transitions.

¹K. Yamanouchi, N. Ikeda, S. Tsuchiya, D. M. Jonas, J. K. Lundberg, G. W. Adamson, and R. W. Field, *J. Chem. Phys.* **95**, 6330 (1991).

²Y.-C. Hsu, M.-S. Lin, and C.-P. Hsu, *J. Chem. Phys.* **94**, 7832 (1991).

³F. Shokoohi, T. A. Watson, H. Reisler, F. Kong, A. M. Renlund, and C. Wittig, *J. Phys. Chem.* **90**, 5695 (1986).

FD12**15 min 11:45**

RADIATIVE AND NONRADIATIVE DECAY OF ELECTRONICALLY EXCITED NCO, SCOTT A. WRIGHT AND PAUL J. DAGDIGIAN, Department of Chemistry, The Johns Hopkins University, Baltimore, MD 21218-2685.

Electronically excited levels in the NCO free radical have been probed using laser fluorescence excitation, in order to observe higher vibronic levels of the $\tilde{A}^2\Sigma^+$ state and to locate the onset of predissociation. Spectra have been recorded over the wave number range 27 400 – 32 900 cm^{-1} , from the $\tilde{A}(0,0,2)^2\Sigma^+ - \tilde{X}(0,0,0)^2\Pi$ band up through the $\tilde{B}(1,0,0)^2\Pi - \tilde{X}(0,0,0)^2\Pi$ band. Vibrational assignments have been made for a number of newly observed $\tilde{A} - \tilde{X}$ bands, and the band origin wave numbers and upper level rotational constants have been derived by comparison of spectra with simulations. Decay lifetimes have been measured for a large number of both assigned and unassigned excited vibronic levels. The onset of predissociation appears to occur at energies slightly below that of the $\tilde{B}(0,0,0)$ level, at 31 750 cm^{-1} . These data also suggest that predissociation occurs at lower energies in bent geometries than in a linear configuration.

FD13**15 min 12:02**

ZEKE-PFI Spectroscopy of the Sodium-Water and Sodium-Ammonia Dimers

Geofferey A. Blake, David A. Rodham, *Division of Geological and Planetary Sciences California Institute of Technology MS 170-25 Pasadena, CA 91125.*

Single-photon ZEKE-PFI experiments have been performed on the Na-H₂O, Na-D₂O, Na-NH₃, and Na-ND₃ clusters in a molecular beam, and two-photon ZEKE-PFI experiments have been performed on the Na-NH₃ and Na-ND₃ clusters. From the single photon spectra the ionization potentials and intermolecular stretching vibrational frequencies of the cluster ions have been determined, as well as the changes in the intermolecular bending vibrational frequencies upon ionization. The intermolecular bending vibrational frequencies of the Na-NH₃ and Na-ND₃ cluster ions were obtained from the two-photon ZEKE-PFI spectra. Partially resolved rotational structure in the spectra will be discussed.

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GOYETTE, T. M. – MF02, RA06,
RG02, FA03, FA04
GRABOW, J. – RG15
GRABOW, J.-U. – MF12, MF13,
FA05
GRANT, E. R. – RC07
GRANT, K. J. – MF01
GREEN, S. M. E. – WH11, WH12
GREGORY, K. J. – RD11
GREV, R. S. – RD11
GRONER, P. – MF07
GRUEBELE, M. – TC04, TC05
GU, J.-P. – WG02
GUARNIERI, A. – FA10
GUENTHER, B. D. – FA04
GUO, B. – MG02
GUO, D. – FC10
GUO, W. – FA04
GUSTAFSON, T. – WG03
GUTOWSKI, M. – WH10
GUTOWSKY, H. S. – TD01

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HAGEMEISTER, F. C. – ME04,
TG01, RB03, RB04
HALL, G. E. – TE03
HALL, J. – TE01
HALONEN, L. – TG11, RH'04
HALONEN, L. O. – FC04, FC12
HALONEN, M. – TG11, RH'04
HAMANN, H. – TE05
HAMILTON, I. P. – TC11
HAN, J. – FB10, FB11
HARJANTO, H. – RC06
HARPER, W. W. – RC06
HARRISON, J. F. – RD04, RD05
HARTMANN, J. M. – WG16
HARTMANN, J. - M. – WG07
HARTZ, C. L. – FB11
HARVEY, B. M. – FD06
HASSANZADEH, P. – TC12
HAWKINS, R. L. – MH08, WG01
HAYES, E. F. – TC08, TC09
HEAVEN, M. C. – ME08, TE'07,
TE'08, TF12, TH02, RH04
HEDDERICH, H. G. – RC07
HELMINGER, P. – MF02, RG02,
RG13
HENRY, A. – RA03
HEPBURN, J. W. – RC03, FD05
HEPP, M. – ME09
HERBST, E. – MF08
HERING, P. – RB09
HERMAN, M. – WG15
HERMAN, M. F. – RH07
HESS, W. – RF09
HIGGINS, J. – WH08, WH09,
WH10, RF05
HIGGINS, K. – TD01, TD02, WF01
HILICO, J. C. – MH12
HILPERT, G. – TD11
HIROTA, E. – MF03, TD08
HIRSCH, G. – WG02, RD03
HODGES, J. T. – ME07
HODJIEVA, E. – WE15
HOLLBERG, L. – FA01, FA06
HOSHINA, K. – RC13
HOUGEN, J. T. – WH05, FC01
HOWARD, B. J. – WF14
HSU, Y. – RC04, RC05
HUENKEMEIER, J. – TA03
HUESTIS, D. L. – RE07
HULLAH, D. F. – TE'04
HUMPHREY, S. – TB05

HUNG, W. – RC12
HURTMANS, D. – RA03
HWANG, M. – TH10

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ICHIHASHI, M. – TC10
IMAJO, T. – MG15, MG16
INUI, S. – MG15
IOANNOU, I. I. – TD05
IRIKURA, K. K. – MF11, TC12,
TH03
ISHIBASHI, C. – RH'07
ITO, Y. – TF03
IZGI, K. C. – RG08

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JABS, W. – WE08
JACKSON, M. – RA12
JACOBSON, M. P. – TC07
JACOBY, C. – RB01, RB09
JACOX, D. F. M. E. – TH03
JACOX, M. E. – TH07
JAEGER, W. – MF14
JAGOD, M. - F. – MG04
JENSEN, P. – TC02, TC03, WG02
JERZEMBECK, W. – RH'04
JIN, P. – MG13, MG14
JOHNS, J. W. – RH'02
JOHNS, J. W. C. – RG05
JOHNSON, P. M. – MG13
JOIREMAN, P. W. – TB03
JORDAN, K. D. – RB04
JOST, R. – FC14, FD01
JOYEUX, M. – FC09
JU, Q. – TB01, TB02
JUDGE, R. H. – RB10
JUNGEN, C. – TF02
JUVAN, K. – FA04
JÄGER, W. – TD09, RG07

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KABLE, S. H. – TF16
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KACHANOV, A. A. – TA12
KALEDIN, A. L. – TE'07, TE'08
KALEDIN, L. A. – ME08, TE'07,
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KALMAR, B. L. – TA11
KAWASHIMA, Y. – MF03, TD08

KEPPLER, K. A. – MH13
KERR, K. E. – MG05
KETKOV, S. Y. – TB07
KHALIL, B. – WG16
KHMELENKO, V. V. – RE16, RF07
KIRMSE, B. – FC14
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KLAASSEN, J. J. – MH03
KLAUS, T. – WE08, RA04
KLEE, S. – MH13, WE03, WE12,
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KLEINERMANN, K. – RB01,
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KLEMPERER, W. – TD01, TD02,
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KREINER, W. A. – RA11
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 MILLER, T. A. – TB12, TC09, TF04,
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 OESTERLING, L. C. - MF02
 OGATA, T. - RG14
 OHASHI, N. - WH05
 OHSHIMA, Y. - WF05, WF13, RC13
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 OKHRIMCHUK, A. G. - TA12
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 OZAKI, Y. - TC10

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PAGE, M. - MH07
 PAK, I. - ME09
 PARMENTER, C. S. - TB01, TB02,
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 PARRISH, J. P. - ME08
 PASINSKI, A. - FD01
 PASINSZKI, T. - MG02, RG07
 PATE, B. H. - MF10, TG06, TG07,
 RH01, FC08
 PATEL, P. - FD11
 PAUL, J. B. - ME05
 PAWLIKOWSKI, M. - FC07
 PEARSON, J. C. - MF08, MF09,
 RG09, FA02
 PELMENEV, A. A. - RE16, RF07
 PERRIN, A. - WA02, WE02
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 PERSON, W. B. - TH12
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 PETKIE, D. T. - MF02, FA03
 PETROV, K. - FA01
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 PHILIPS, L. A. - TG15, WE10
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 PICKETT, H. M. - RG09, FA02
 PILGRIM, J. S. - RE04
 PINE, A. S. - MH01, MH02, TG03,
 FC05
 PITZER, R. M. - RD06, RD07, RD08
 PLÍVA, J. - FC05
 PODMARKOV, Y. P. - TA13
 POGORELOV, V. - WE15, RH'08

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 POPOV, E. A. - RE16, RF07
 POWERS, D. E. - TB12, TF04, TF14,
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 POYNTER, R. L. - RG09
 PRATT, D. W. - TB05, TB06, TB08,
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QIAN, C. X. W. - TE'05

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 REDDIC, J. E. - RE03, RE04, FD04
 REHLE, D. - MH05
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 SASADA, H. - ME12, RH'07
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 SCHERBAKOV, A. - RH'01
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 SEARS, T. J. - MG13, MG14, TE02,
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 SEISER, N. - ME13
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 SHKRUNIN, V. – WE14
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 SICKAFOOSE, S. M. – RG10, RG11, RG12
 SIEBER, M. K. – TE'01
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XIE, X. S. - MA03
XIN, J. - TF07
XU, L. - MF05, TG03
XU, L.- H. - TG15
XU, Y. - FB01, FB02

Y

YAMADA, K. M. T. - RA05
YANG, M. - TF11, RC10
YANG, X. - TF10

YEH, P. - WE05

YIANNPOULOU, A. - WH02
YOUNG, M. A. - RH02
YOUNG, S. H. - RG13
YUKIYA, T. - RA09, RE15
YURTCHENKO, S. N. - WG12
YURTSEVEN, H. - WG13

Z

ZEE, R. D. V. - ME07
ZEE, R. J. V. - TH14, RF06
ZERBETTO, S. C. - FA07, FA08
ZERNER, M. C. - TH14

ZGIERSKI, M. Z. - FC07
ZHANG, K. - MG02
ZHANG, K.- Q. - MG01
ZHANG, Y. - RF01
ZHANG, Z. - RD08
ZHAO, C. - RC02, RC03
ZHAO, K. - RD07
ZHAO, Z. - TB01
ZIKRATOV, G. - RE08
ZIMERING, B. - TE04
ZINK, L. R. - FA07, FA08
ZIURYS, L. M. - WF01, WF02
ZWIER, T. S. - ME04, TG01, RB02,
RB03, RB04

NOTES

NOTES

Information

ACCOMMODATIONS: The check-in for dormitory accommodations is located in Drackett Tower (F) on Curl Drive. Drackett Tower will open at 7a.m. Sunday, June 9, and remain open 24 hours a day through the Symposium. The dorm dining room will open Monday morning for breakfast. Meal plans may be purchased upon registration.

Other hotels close to campus include: Fawcett Center, 2400 Olentangy River Rd., 292-3238; Holiday Inn on the Lane, 328 W. Lane Ave., 294-4848; Red Roof Inn, State Route 315 & Ackerman Rd., 267-9941; Ramada University, 3110 Olentangy River Rd., 267-7461; Best Western, 3232 Olentangy River Rd., 261-7141; Parke Hotel, 3025 Olentangy River Rd., 267-1111.

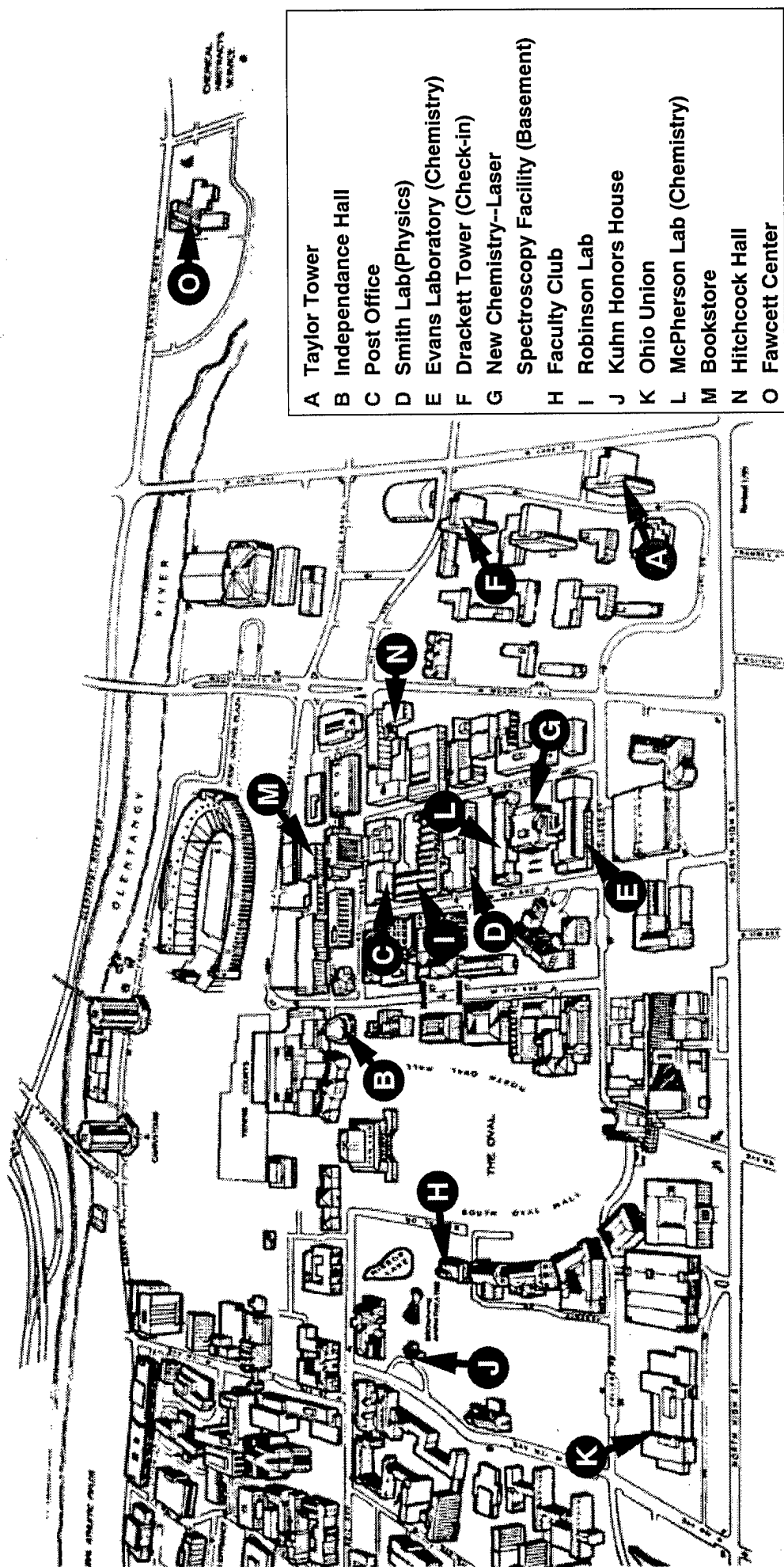
MAIL: Address your mail for delivery during the Symposium to: c/o MOLECULAR SPECTROSCOPY SYMPOSIUM, Department of Physics, The Ohio State University, 174 West 18th Avenue, Columbus, Ohio, 43210, U.S.A. FAX number - (614) 292-1948, Telephone number - (614) 292-2569.

PARKING: Parking permits are available **only** from the check-in desk at Drackett Tower. Due to construction in the Tuttle-Woodruff parking lot, these permits allow you to park in the St. John Arena parking lot only. The permit must be displayed on the front windshield of your car. NOTE that Neil Avenue is closed from Lane Avenue to Woodruff. Please follow all traffic rules to avoid the issuance of tickets.

REGISTRATION: The Registration Desk will be located in Room 1036, Physics Laboratory. It will be kept open between **4:00-6:00 p.m. Sunday**, and **8:15a.m. - 4:30p.m., Monday through Friday**. Those who have prepaid their registration and who are staying in the dorms will receive their registration packet at dormitory check-in. If you have prepaid your registration but are not staying at the dorms, pick up your packet at the Registration Desk. **NOTE: If the dates of your stay have changed since preregistering, please settle your account at the Drackett Tower front desk before you leave.**

LIABILITY: The Symposium fees DO NOT include provisions for the insurance of participants against personal injuries, sickness, theft or property damage. Participants and companions are advised to take whatever insurance they consider necessary. Neither the Symposium organizing committee, its sponsors, nor individual committee members assume any responsibility for loss, injury, sickness, or damages to persons or belongings, however caused.

AUDIO/VIDEO INFORMATION: Overhead projectors will be available for each session. Since use of **slide projectors** has been essentially non-existent in recent years, they **will no longer be available** routinely. Anyone needing a slide projector, or any other special audio/video equipment, should contact the Symposium office as soon as possible.



- A Taylor Tower
- B Independence Hall
- C Post Office
- D Smith Lab (Physics)
- E Evans Laboratory (Chemistry)
- F Drackett Tower (Check-in)
- G New Chemistry--Laser Spectroscopy Facility (Basement)
- H Faculty Club
- I Robinson Lab
- J Kuhn Honors House
- K Ohio Union
- L McPherson Lab (Chemistry)
- M Bookstore
- N Hitchcock Hall
- O Fawcett Center

51ST OHIO STATE UNIVERSITY INTERNATIONAL SYMPOSIUM ON MOLECULAR SPECTROSCOPY
JUNE 10-14, 1996

	MONDAY JUNE 10TH 8:45AM	TUESDAY JUNE 11TH 8:30AM	WEDNESDAY JUNE 12TH 8:45AM	THURSDAY JUNE 13TH 8:30AM	FRIDAY JUNE 14TH 8:30AM
AUDITORIUM INDEPENDENCE HALL	MA. PLENARY SESSION RAO AWARDS COBLENTZ AWARD & LECTURE		WA. PLENARY SESSION		
ROOM 1153 SMITH LAB		TA. SYMPOSIUM: ABSORPTION SPECTROSCOPY		RA. SYMPOSIUM: COHERENT IR	FA. SYMPOSIUM: COHERENT IR
ROOM 1009 SMITH LAB		TB. ELECTRONIC (LARGE)		RB. ELECTRONIC (LARGE)	FB. INFRARED: JET & BEAM
ROOM 1005 SMITH LAB		TC. THEORY		RC. RADICALS	FC. THEORY
ROOM 1008 EVANS LAB		TD. MICROWAVE		RD. THEORY	FD. ELECTRONIC (SMALL)

1:30PM

ROOM 1153 SMITH LAB	ME. SYMPOSIUM: ABSORPTION SPECTROSCOPY	TE. SYMPOSIUM: ABSORPTION SPECTROSCOPY TE'. ELECTRONIC (SMALL)	WE. INFRARED	RE. ELECTRONIC (SMALL)	
ROOM 1009 SMITH LAB	MF. MICROWAVE	TF. RADICALS	WF. MICROWAVE: RADICALS & IONS	RF. MATRIX & CONDENSED PHASE	
ROOM 1005 SMITH LAB	MG. RADICALS & IONS	TG. JET & BEAM	WG. THEORY	RG. MICROWAVE	
ROOM 1008 EVANS LAB	MH. INFRARED	TH. MATRIX & CONDENSED PHASE	WH. ELECTRONIC (SMALL)	RH. JET & BEAM RH'. INFRARED	